

# EVERYDAY CHEMISTRY





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# EVERYDAY CHEMISTRY

BY

J. R. PARTINGTON, M.B.E., D.Sc.

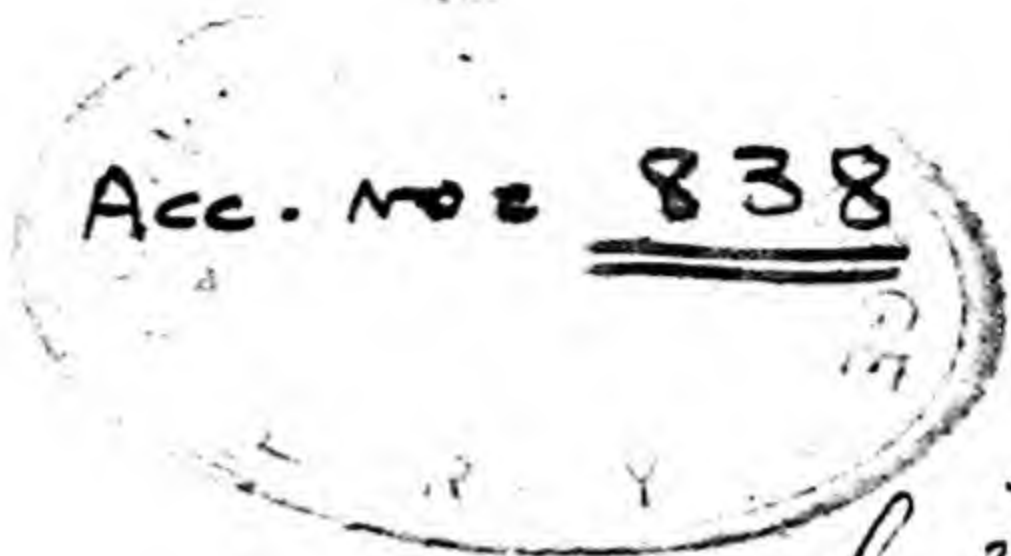
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF LONDON  
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## EXTRACTS FROM THE PREFACE OF THE FIRST EDITION

THE present work provides an elementary text-book, of the standard of School Certificate and Matriculation examinations, or a little beyond, suitable for use in schools, and at the same time gives an account of those principles and applications of chemistry which are of importance and interest in everyday life. The range of subjects is, therefore, necessarily somewhat wider than the requirements of the syllabuses of the examinations mentioned, but these syllabuses are fully covered so far as the theoretical side is concerned. No attempt has been made to provide a course of practical work. The extra material is chiefly that concerned with organic chemistry. The importance of this subject in daily life is such that no book with the title of *Everyday Chemistry* could possibly omit to deal with it.

The method of treatment aims at giving an account of the whole subject which will enable those who have a very elementary knowledge of chemistry to follow the recent advances in the science, and at the same time providing a clear and concise statement of the fundamental facts and theories of chemistry which will be suitable as a systematic course for students.

The division of the book into three parts: (I) Historical and Theory, (II) Non-Metals, and (III) Organic Chemistry and Metals, was adopted after careful consideration as on the whole most convenient for the readers for whom the book is intended. In the school, each teacher will decide which order of treatment best meets the needs of the class, and the study of Part II. may be begun after the earlier sections of Part I. have been dealt with. Since the book is intended to provide a course of reading which will supplement and extend what has been dealt with in the class-room, and laboratory, this method of arrangement will, it is believed, be found useful.

An attempt has been made to include some of the most recent advances in chemistry, both in theory and practice, and the treatment throughout aims at conforming with the present stage of development of the science. Care has been taken, however, not

to omit those elementary and fundamental parts of the subject which must form the basis of every successful course of study.

In providing material for the numerous illustrations the author has had great assistance from manufacturers and others. In most cases the sources of such illustrations are given in the titles. He wishes to thank Messrs. Bell and Sons for permission to use illustrations from his book, *The Composition of Water*, for Figs. 93 and 94.

The author, in conclusion, wishes to express his deep indebtedness to Sir Richard Gregory for his valuable advice and assistance both in planning the character and scope of the work and during the course of its passage through the press. Mr. A. J. V. Gale has made many helpful suggestions and gave valuable assistance during the proof-reading.

J. R. PARTINGTON.

## PREFACE TO THE SECOND EDITION

ALTHOUGH many parts of the book were revised and brought up-to-date in successive reprintings, the alterations made in the present issue seemed to warrant its description as a second edition. Many parts have been rewritten, and changes have been made in several of the illustrations. The subjects of Chapters IV to VI have now been extended in the author's *Short History of Chemistry* (second edition, Macmillan and Co., 1947), but the present text has been retained and modified as an introduction to these topics. Considerable changes have been made in Chapter XXIX, in conformity with recent advances in the subjects with which it deals. It is hoped that the book in its revised form may continue to find approval in its field.

J. R. PARTINGTON.

February, 1947.



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NOTE.—*Chapters marked with an asterisk deal principally or entirely with subjects outside the scope of the Matriculation Syllabus, as also do paragraphs in other chapters marked in the same way.*

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*PART I*  
CHEMICAL HISTORY AND THEORY





# CHAPTER I

## INTRODUCTION

**Varieties of materials in everyday life.**—One of the most evident facts of everyday experience is that there are very many things around us which differ completely in their essential characters, or properties. A house is constructed of various kinds of stone, bricks, different woods, iron, concrete, slates, tiles, plaster, mortar, and glass. The furniture and fittings inside consist of other kinds of wood, of different metals such as lead, copper, brass, bronze and aluminium; and in the various rooms will be found miscellaneous articles made of such materials as ebonite, celluloid, porcelain, wool, cotton, silk, tinsplate, silver and gold, together with various kinds of food, oil, coal, drinking water, candles and gas. In the world outside there are still other things. The contents of the druggist's shop, of the oil and colour store, and of the garage, the dyes used in relieving the monotony of our surroundings, paints, varnishes, enamels, explosives, and the bitumen on the roads are all different materials. The world of Nature, with its rocks, minerals, plants and animal life, presents another picture of the apparently endless variety of materials which we encounter at every turn.

These differences exist, as we realise, quite apart from any particular shape or size which has been given to the objects. An oak chair consists of the same kind of wood as an oak table, but of different wood from that of a mahogany chair. The wool of different garments is essentially the same material and quite different from the cotton of the clothing worn in warmer weather. Even a thick cotton garment is not so warm as a thin one of wool, and the textures also differ.

We summarise these differences in essential properties by saying that **things may differ in composition**. Sugar and salt are two materials of different composition; a lump of sugar and powdered sugar are two different forms of the same material.

**Chemical qualities.**—Some things are formed by simply mixing together others of simpler composition, as mortar from lime, sand and water. In other cases a more marked change in properties occurs, as when glass is produced by fusing together sand, lime and soda, or when soap is made by boiling fat or oil with soda rendered caustic by treatment with lime. This second type of change is a chemical change, as distinguished from a physical change produced by mere mixing. If a material can be produced by putting together two or more other materials it will usually be more complicated than these, and we can in this way get some information about its composition. Glass, we may expect, will contain materials present in sand, lime and soda.

Another way of finding the composition of a material is to take it to pieces, as it were, and resolve or **analyse** it into the simpler materials of which it is composed. In some cases it is fairly easy to break down one kind of material into simpler ones, but difficult, if not impossible, to put these materials together again so as to reproduce the original substance. For example, when sugar is heated fairly strongly it chars; steam and other gases are given off, and a black mass of charcoal remains. Although it is possible to produce sugar again from water and charcoal, yet this requires the greatest skill of the chemist and the use of apparatus and materials found only in the chemical workshop or laboratory. Even the chemist has not succeeded in putting together the parts of burnt meat so as to reproduce the original flesh. He cannot change a cooked egg into a raw egg, or an oak into an acorn and the materials taken from the air and soil when the acorn changed into the oak.

The chemist of to-day can do wonderful things but there are innumerable changes going on all around us in Nature which cannot be imitated in the chemical laboratory, just as there are numerous operations in the laboratory which do not appear to occur at all in Nature. Even when the chemist can make the things which plants or animals produce, he has often to do it by totally different methods, involving the application of great heat or pressure, or the use of corrosive or poisonous chemicals which are never found in plants, animals or rocks.

The chemist, however, is always hoping that by further work in the laboratory he will acquire new powers and will be able to produce artificially many things which Nature is able to elaborate but which are yet beyond his skill. Since the beginning of the nineteenth century the chemist has learnt how to obtain in



the laboratory many things the production of which was formerly thought to be beyond human agency.



Chemical Laboratory

FIG. 1. FIG. 2. FIG. 3. FIG. 4. FIG. 5.

We may now review briefly some of the regions of scientific life in which chemistry plays an important part.

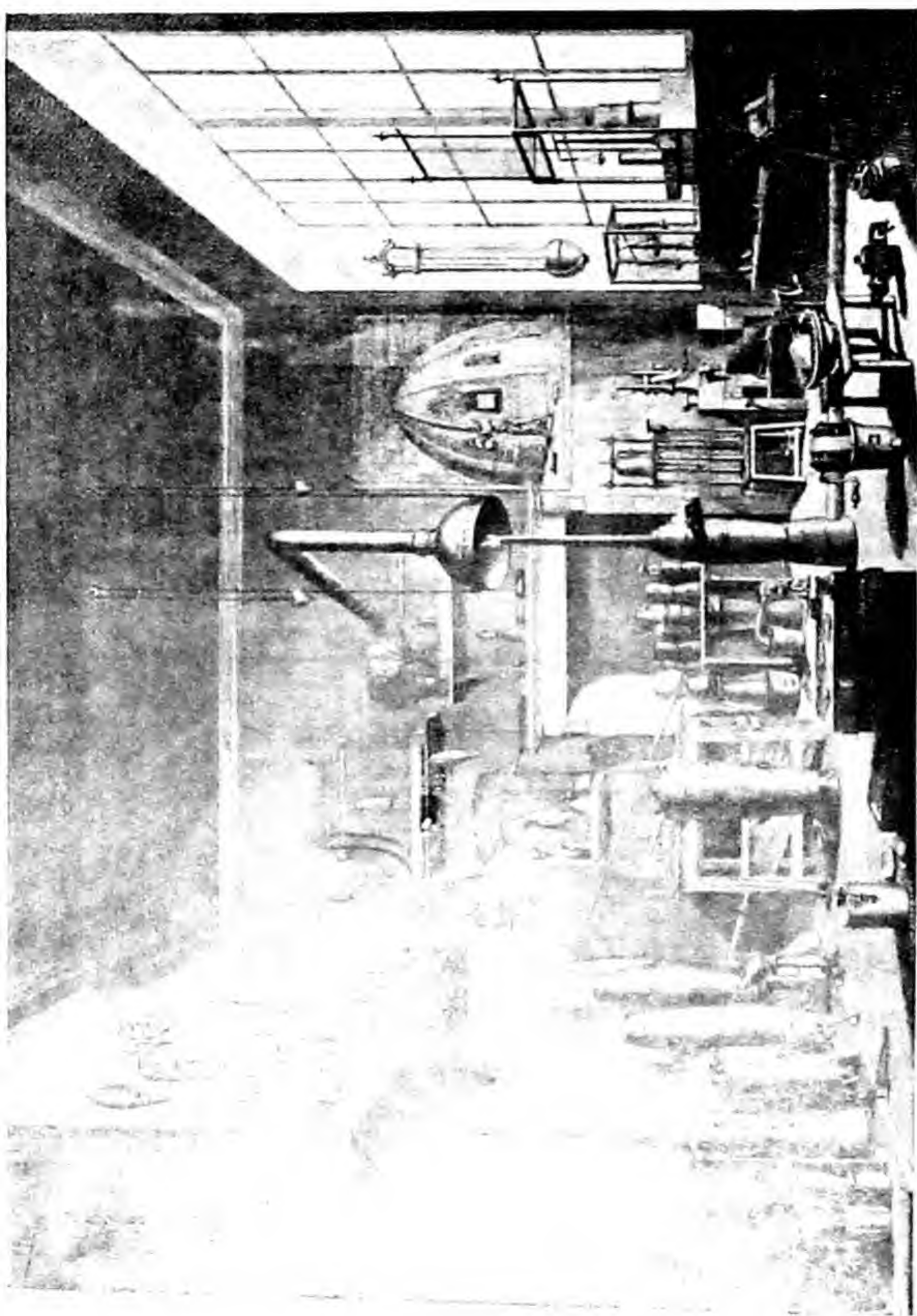


FIG. 2.—A CHEMICAL LABORATORY OF THE EIGHTEENTH CENTURY.

MUCH OF THE APPARATUS IS LIKE THAT USED BY THE ALCHEMIST.



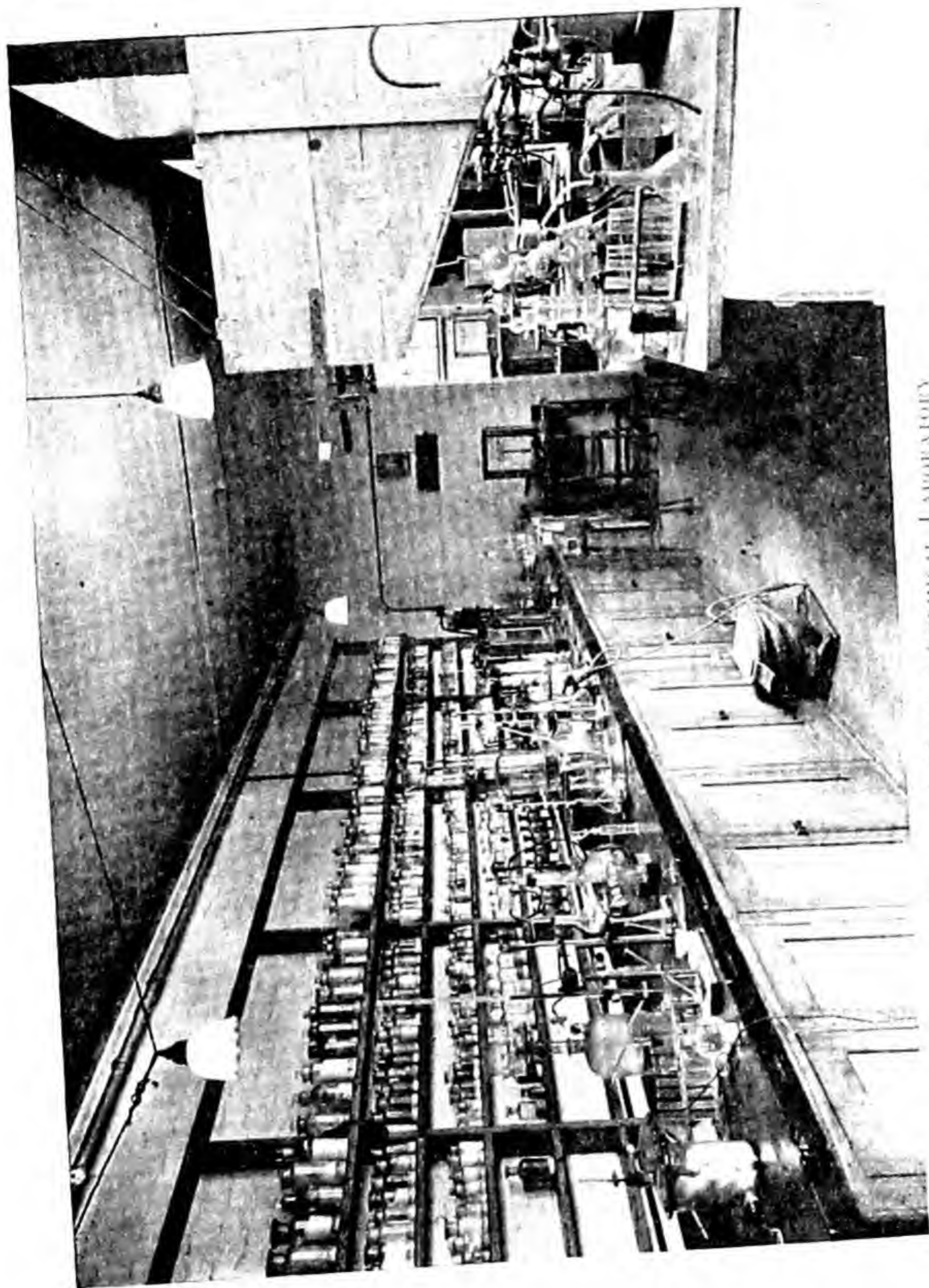


FIG. 3.—A MODERN CHEMICAL LABORATORY

NOTE THE ARRANGEMENT OF THE BENCHES AND THE SPECIFICALLY DESIGNED CABINETS FOR THE STORAGE OF THE MATERIALS AND THE EQUIPMENT.

**Dyes.**—The blue colouring matter of the dye indigo, which was obtained from the indigo plant by the Egyptians more than 4000 years ago, was produced artificially in 1870 by von Baeyer, and a large part of all the indigo now used is made in chemical factories. It is identical with the blue colouring matter of natural indigo and is not an imitation of it. By studying the composition of the blue colouring matter of indigo and finding



**Drugs.**—To many people, and also in the eyes of the law, a 'chemist' is one who is qualified to make and sell drugs, although he should properly be called a pharmacist. Nevertheless, the chemist has had a great deal to do with the discovery of drugs. In former years many drugs used by medical men were of vegetable origin. In curing fevers the bark of the Cinchona tree began to be used about 1650. This bark contains some active constituents mixed with a large mass of inert and useless woody matter, and as the proportion of active substances varies, the action of the dose of bark was erratic and not easily controlled. In 1820 two French chemists, Pelletier and Caventou, isolated by chemical processes from the bark a crystalline substance called **quinine**, and the pure drug is now always used. Quinine has not yet been prepared artificially but a number of other substances belonging to the same class (called **alkaloids**) have been, and there is every reason to suppose that quinine will also, some day, be made by the chemist.

Many artificial drugs are better for some purposes than the natural ones which they replace. The dentist uses a local anaesthetic to allay the pain of an operation, and this was formerly **cocaine**, which is an alkaloid. This drug, however, has undesirable after-effects; by examining its composition the chemist imagined that he could produce something which would do the work of cocaine and yet not have its objectionable properties, *e.g.*, its action on the heart. The result of his experiments was the production of substitutes, such as **stovaine** and **novocaine**, which are now replacing cocaine. To prevent bleeding, which does not occur when cocaine is used but does with novocaine, another drug called **adrenalin** is added to the novocaine. Adrenalin was at first obtainable only from certain animal glands but it can now be prepared by the chemist.

Most diseases are produced by minute living organisms called **bacteria** (Figs. 5 and 6), which it is the object of disinfection to destroy. Many kinds of **disinfectants** are used. Chlorine is a powerful disinfectant; hydrogen peroxide is milder, but is especially useful because when diluted with water it is not poisonous. Some kinds of tooth-paste contain substances which, when brought in contact with water, liberate hydrogen peroxide. Other disinfectants contain phenol ('carbolic acid') and related substances, called **cresols**, obtained from coal-tar.

Some diseases, such as malaria and sleeping sickness, are caused not by bacteria but by organisms called **trypanosomes**,



which enter the blood and go through complicated life-processes. There are certain drugs made chemically which have the property

of killing trypanosomes without injuring the cells of the human body. These include compounds of antimony.

It may also be mentioned here that the processes taking place in the body, such as digestion, are largely chemical changes brought about by specific substances called *enzymes*. Much light has been thrown on physiology by the chemical study of these changes, and biochemistry is now a large and important branch of chemistry.



FIG. 5.—*Bacillus Anthracis* PRODUCING ANTHRAX.

**Metals.**—Examples of the practical everyday applications of chemistry may be found in the production and use of metals.

The name metal is derived from a Greek word which occurs in Herodotos (485-425 B.C.) with the meaning of a *mine*; it afterwards came to mean things dug from mines, *i.e.* *ores*, from which what we now call *metals* are obtained. Until the middle of the nineteenth century the only metals in common use were copper, iron, tin, zinc, and the mixtures or alloys called bronze (copper + tin) and brass (copper + zinc). Steel is only a form of iron containing small amounts of carbon. All these metals have been known and

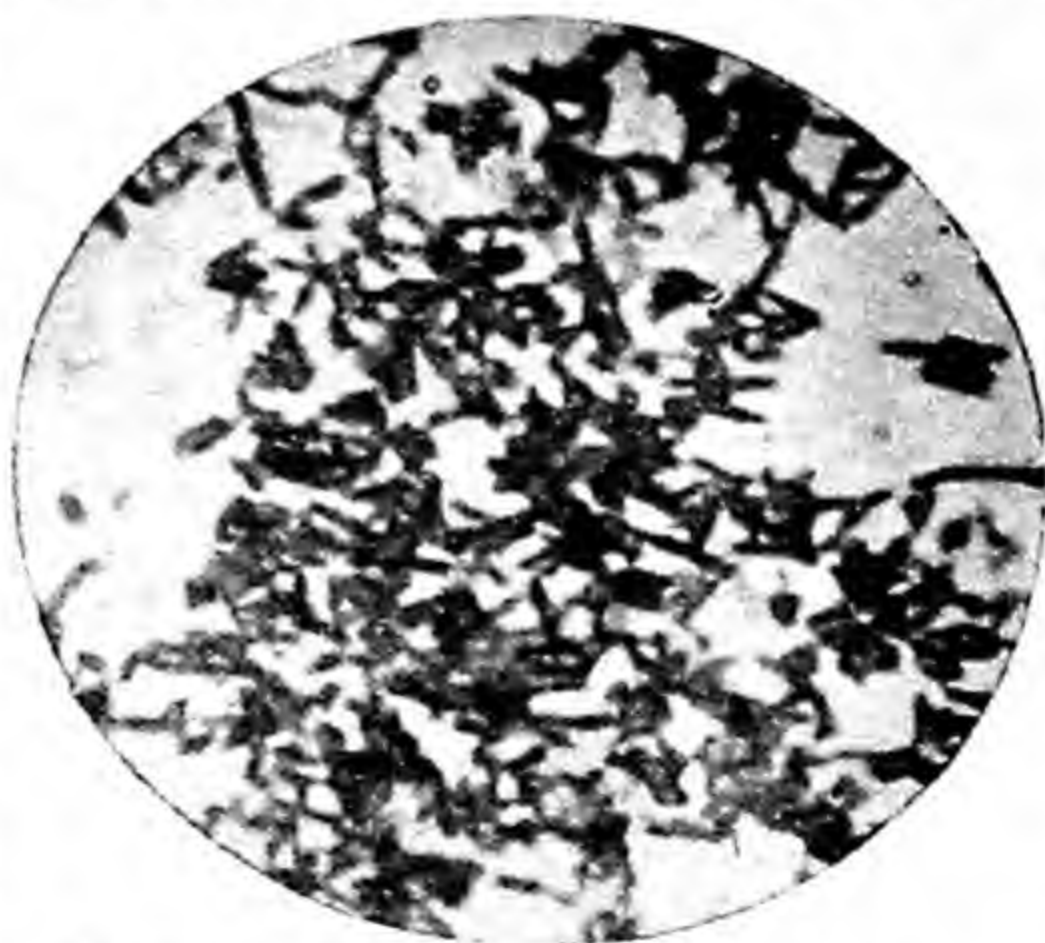


FIG. 6.—BACILLI RESPONSIBLE FOR THE DISEASE OF DIPHTHERIA.

used for thousands of years—copper probably for over five



thousand years. The metal aluminium, a constituent of clay, was discovered in 1828 and was at first very rare and valuable. In 1854 the French chemist Deville discovered a method by which it could be manufactured, and in 1886 Hall in America and Héroult in France independently devised new processes depending on the use of electricity by means of which aluminium can be made cheaply in large quantities, and the metal is now extensively used. It is not yet possible to extract aluminium from clay: most of it is obtained from the mineral bauxite, which must first be carefully purified.

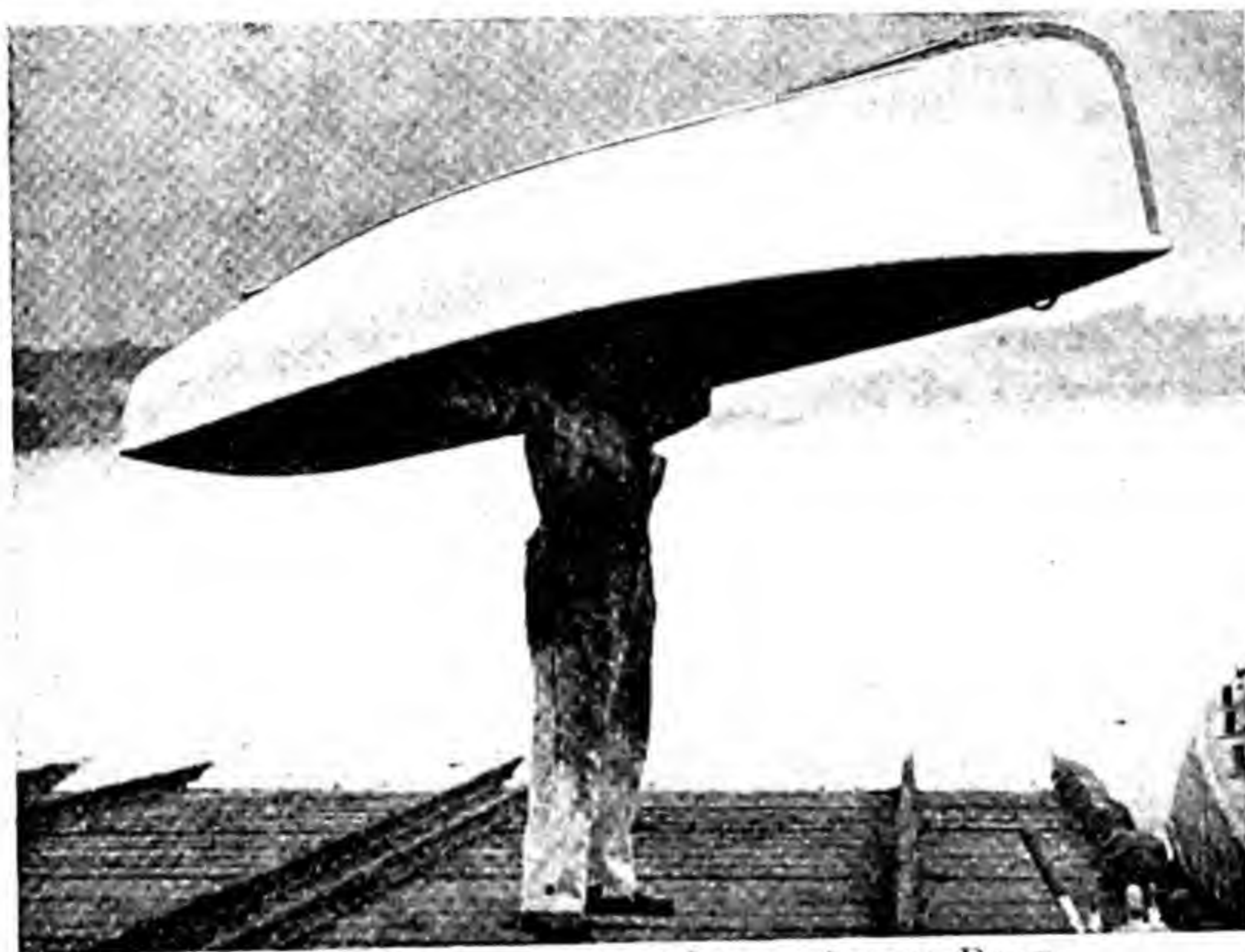


FIG. 7.—' BIRMABRIGHT ' LIGHT ALLOY BOAT.  
(Birmabright Ltd., Birmingham.)

Another metal which was not known until early in the nineteenth century is magnesium, which is now also obtained in fairly large quantities by an electrical method. An alloy of magnesium with aluminium has great strength and is very light, being only about twice as heavy as an equal bulk of water, whilst steel is about eight times as heavy as water. Such light and strong alloys are of great value in aeroplane and other engineering construction (Fig. 7).

The metals tungsten and molybdenum, until quite recently

only curiosities in chemical laboratories, are used in making electric lamps (Fig. 8A) and wireless valves, and alloyed with iron in

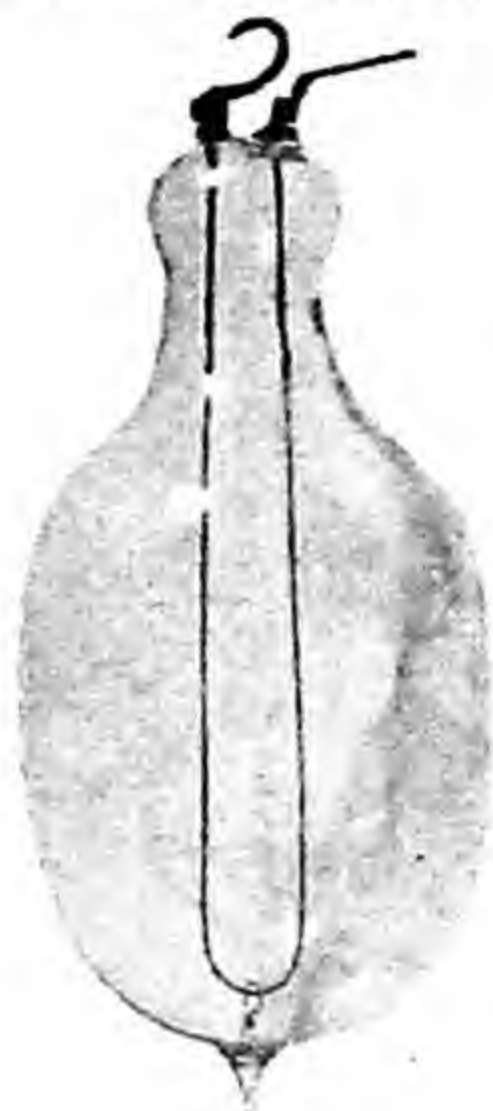


FIG. 8.

100 V. 400 C.P.  
CARBON FILAMENT  
LAMP, c. 1896. (STILL  
WORKING.)

(By courtesy of G.E.C.)

special steels. Many other 'rare' materials, like selenium, could be produced in fairly large quantities if any use could be found for them. An apparatus for turning off street lamps automatically contains selenium. The metal beryllium, which occurs in emeralds, is lighter even than aluminium, is hard and strong and is not easily tarnished. Its compounds are used in gas mantles and the metal itself is finding industrial uses in the form of alloys with other metals.

Many valuable metals are produced by mixing, or alloying, simple metals. Bronze and brass are alloys which have been used for centuries. Printers' type consists of lead, antimony and tin, and this alloy has the property of expanding slightly when the fused metal solidifies, so that sharp impressions of the moulds are obtained. Stainless steel is an alloy of iron with chromium and nickel, and many special steels contain iron alloyed with such metals as tungsten, molybdenum, vanadium, and cobalt, which were

scarcely known a few years ago. Chisels, lathe tools, parts of motor cars, railway tracks and steel for bridges all make use of these alloy steels. The gear wheels in a motor car, for example, have to stand rather rough usage, and are made of special steel. The valves in the engine, again, which are exposed to very high temperatures, are made from another special steel, as are the front axles.

Metals have been replaced for many purposes by plastics, which are artificial products of various types.

The so-called Bakelite plastics, made from phenol and formaldehyde (p. 510), are used for containers and many other purposes; when made up in laminated

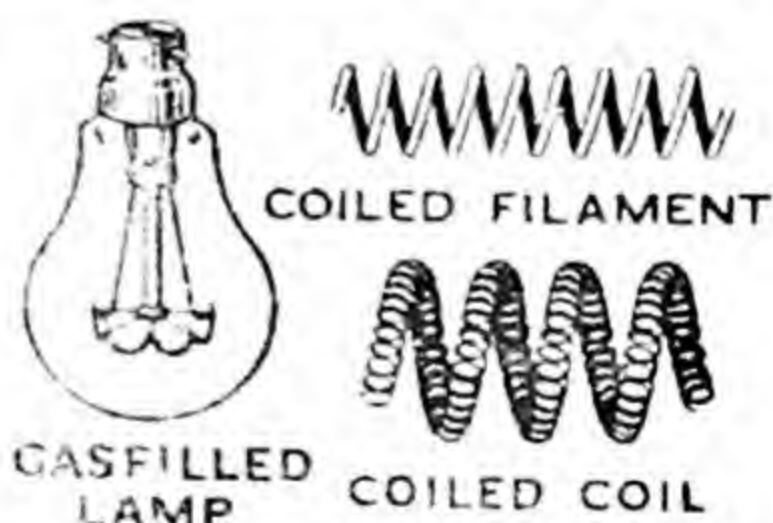


FIG. 9A. MODERN ELECTRIC LAMP.

Science Museum, London. Copyright.



form, by impregnating layers of paper, fabric, or other woven materials with a solution of the plastic, super-imposing them, and

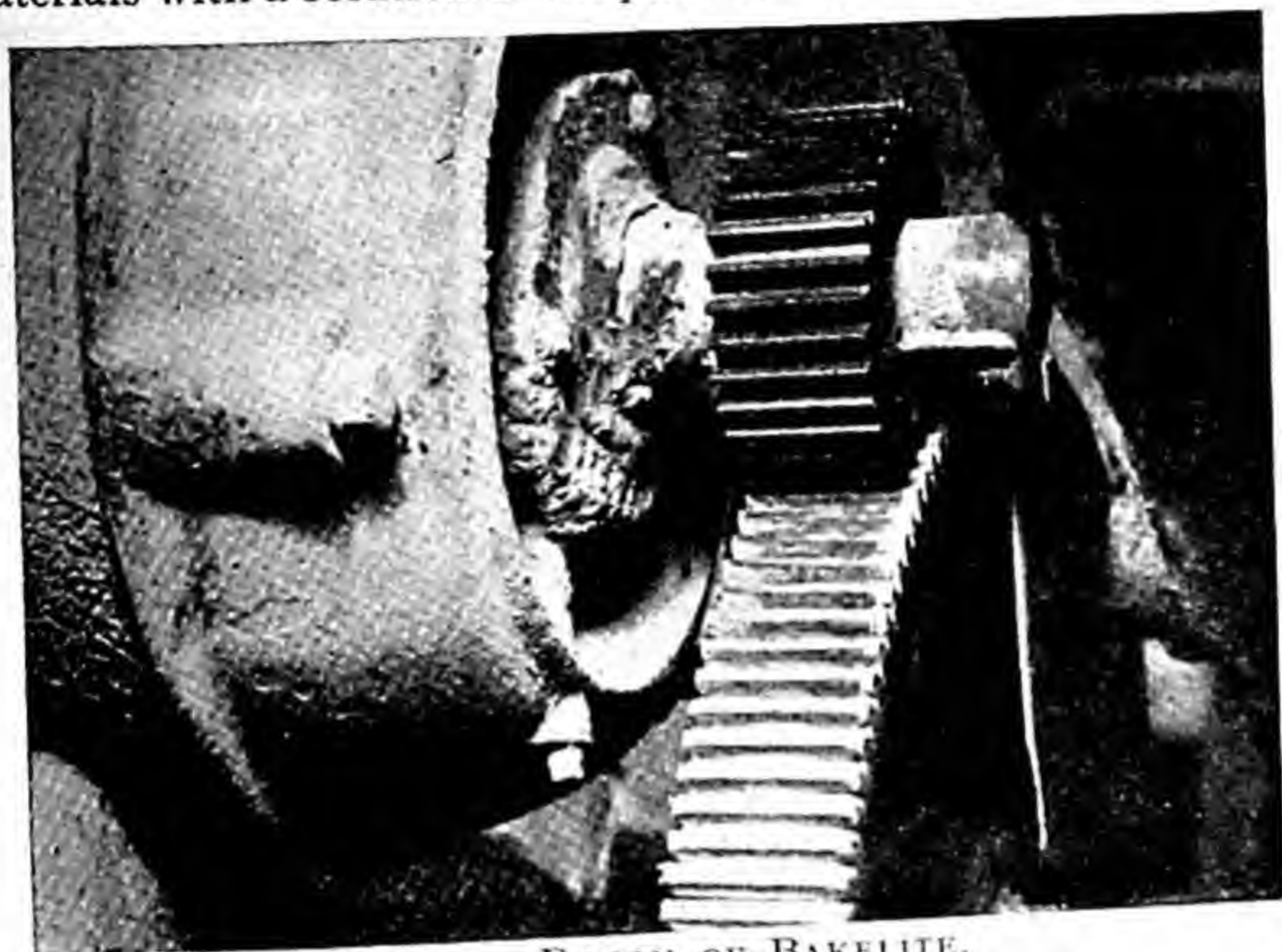


FIG. 9.—PINION OF BAKELITE.  
SILENT GEAR MATERIAL MESHED WITH A STEEL WHEEL.  
(Bakelite Ltd.)

subjecting them to heat and pressure, a material is formed which may have very good mechanical and electrical properties. By using a cotton, or especially linen, reinforcement, a material of very high tensile strength is formed. Such laminated material has been used for gear wheels (Fig. 9). Other types of plastics (p. 538) are transparent and replace glass, over which they have the great advantage of toughness and shock-resisting properties. These have been used for aeroplane windows.



FIG. 10.—'WELVIC' (POLYVINYL CHLORIDE)-COVERED ELECTRIC CABLE. (See p. 538.)  
(Imperial Chemical Industries Ltd.—Plastics Division.)

Other plastics are used as electrical insulators (Fig. 10). The plastic industry, which is practically entirely a branch of applied chemistry, has made enormous strides in comparatively recent times, and its products are now seen and used in all walks of life. It is hardly an exaggeration to say that in many directions modern life has been transformed by the work of the chemist.

**Early knowledge of metals.**—In the early period of his life man was not acquainted with the use of metals: his implements were made of stone, horn or bone. The first metal known was



FIG. 11.—SUMERIAN COPPER SCIMITARS FROM TELLO.  
ABOUT 3000 B.C.

probably gold, which occurs in the native metallic form and would attract attention by its colour and lustre. Gold ornaments are found with remains of polished and worked stone implements dating back to a very early period, the so-called Neolithic Age. The next metal known was probably copper, and some think it was known even before gold in Egypt. Copper appears in the earliest remains in Egypt and in Mesopotamia in the form of cast objects dating back to before 3000 B.C.



FIG. 12.—SILVER VASE  
OF ENTEMENA, RULER OF  
LAGASH 2850 B.C.  
WITH ITS COPPER STAND.  
(The Louvre, Paris.)

The earliest known working in metals appears in three places: in Egypt, in Mesopotamia (the modern Iraq), and in the island of Crete, in the Mediterranean. Egypt and Mesopotamia are rivals in the claim for the origin of the working of metals.

The ancient inhabitants of Mesopotamia, the Sumerians, had an advanced culture at least as early as the First Dynasty in Egypt,



and were expert in the working of gold, silver, copper and bronze from about 3500 B.C. Very fine specimens of early



**COPPER BULL'S HEAD.**  
TELL EL 'OBEID, EARLY SUMERIAN,  
ABOUT 3000 B.C.  
(British Museum.)



**FIG. 13. GOLD BULL'S HORN.**  
TELL EL 'OBEID, EARLY SUMERIAN,  
ABOUT 3000 B.C.  
(British Museum.)

Sumerian metalwork were found on the site of Ur of the Chaldees, where there are the remains of a great temple. The copper scimitars shown in Fig. 11, the finely engraved silver vase shown in Fig. 12, and the copper and gold objects in Fig. 13, are good examples of early Sumerian work.

The ancient Egyptians probably obtained their copper from the ores in the peninsula of Sinai, which are very easily reduced to the metal,

and these ores are known to have been worked at a very early period. Copper was in use in the Predynastic Period, *i.e.* before 3400 B.C.

Fig. 14 shows an early Egyptian vessel of copper (about



**FIG. 14.—EARLY DYNASTIC EGYPTIAN  
COPPER VESSEL, ABYDOS.**  
(From Evans' *Palace of Minos at Knossos*.)

3000 B.C.) and Fig 15 some early metal objects of a slightly later period, including a lump of iron. Lead is represented by the archaic statuette shown in Fig. 16. Gold and (more rarely)

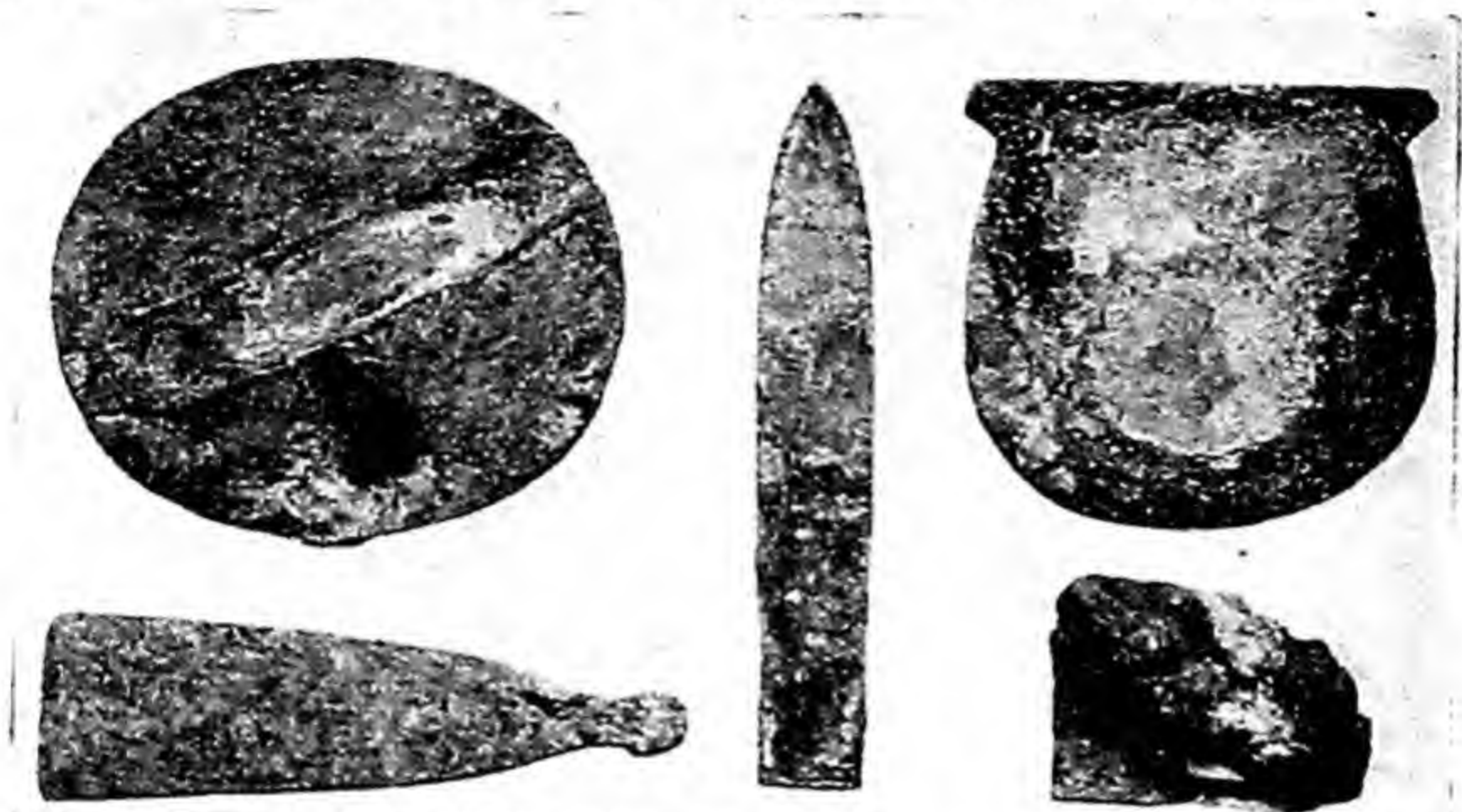


FIG. 15.—COPPER MIRROR, COPPER TOOLS, AND (LOWER RIGHT-HAND CORNER) LUMP OF IRON FOUND AT ABYDOS (2700-2500 B.C.).  
(British Museum.)



FIG. 16.—LEAD STATUETTE FOUND IN EGYPT, FIRST DYNASTY, 3400 B.C.  
(British Museum.)



FIG. 17.—MINOAN GOLD CUP, about 1500 B.C.



silver objects also occur. Iron has been found very sparingly in Predynastic Egyptian remains.

Copper also occurs in the remains at Knossos, and other sites in the island of Crete, which was the centre of an old civilisation known as the Minoan: this copper dates back to about 3000 B.C. and may have come from the island of Cyprus. The Cretans probably learnt the use of metal from Egypt, with which they were in relation from the earliest times. The beautiful gold cup found at Vaphio, shown in Fig. 17, is regarded as of later Minoan origin, and the very advanced stage of pottery working in Minoan times is illustrated by the vase shown in Fig. 18.

A later stage of the Minoan culture on the mainland was the so-called Mycenaean, represented by the finds of great stores of gold objects in tombs at Mycenae, and by remains at Tiryns, including blue glaze (*kuanos*). These belong to the period of 1500-1200 B.C. and the Mycenaean culture (which is that described by Homer) preceded the introduction of iron, which began with classical Greece. The use of iron came in with a new people, who destroyed the Minoan culture.

A great advance in metal working was possible with the invention of bronze, which is an alloy, or mixture, of copper and tin. Bronze usually appears later than copper, and in several places about the same time. The earliest Egyptians were expert in working metals, as the remains of their craft show. There are representations of early metal working in wall inscriptions, such as the copper working shown in Fig. 19 and the goldsmiths shown in Fig. 20. The operations shown in Fig. 19 were formerly thought to represent glass-blowing.

The earliest Egyptian bronze is generally stated to be that found by Petrie in the Fourth to Sixth Dynasty remains at



FIG. 18.—MINOAN POLYCHROME POTTERY WITH FLOWERS AND FOLIAGE, FROM PALAIKASTRO, 2200 B.C.

(From Evans' *Palace of Minos at Knossos*.)

Medum, dating to about 3000 B.C., although a piece of true bronze from a tomb of the First Dynasty (*c.* 3400 B.C.) is described by Mosso. At Ur, good bronze of 3500 B.C. was found. The source of the tin used in making these early bronzes is a problem since tin is not found in many places, and some modern sources (*e.g.*, the Malay Peninsula) were not likely to have been known to the ancients. Some archaeologists consider that even this earliest tin came from Britain—the Islands of the Kassiterides (*kassiteros* was the Greek name for tin), perhaps the English coast of Cornwall, from whence tin was certainly shipped by the Phoenicians in later times, but the generally

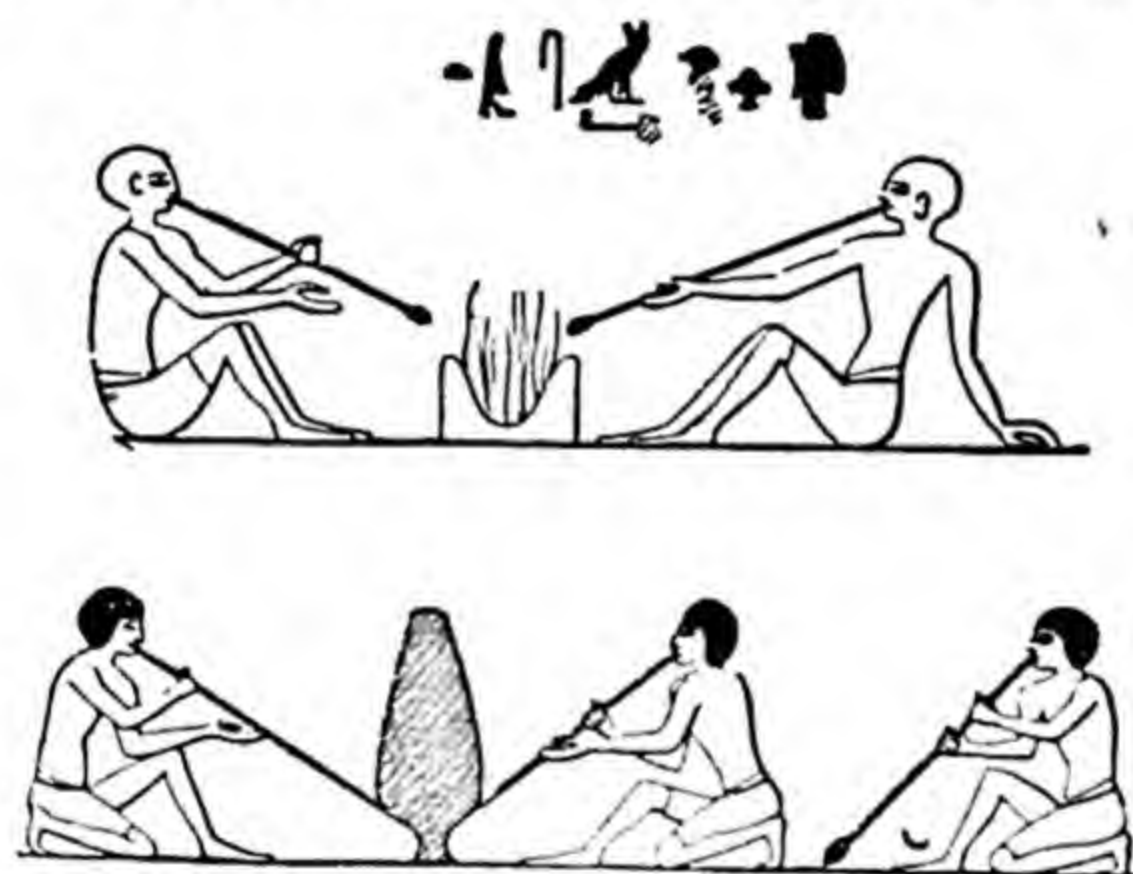


FIG. 19.—EGYPTIAN METAL WORKING.

*Upper*: BLOWING THE FIRE WITH CLAY-TIPPED REED BLOWPIPES; INSCRIPTIONS, BENI HASSAN, 1900 B.C. *Lower*: FASHIONING A COPPER VASE; THEBES, ABOUT 1550 B.C.

accepted theory is that the tin came from mines in Persia which are mentioned by Strabo, although it is true that there is no tin there at the present day, nor does there seem to have been any for a very long time. The mines may have been worked out at an early period.

The metals iron, silver and lead were also known in Egypt, soon after copper and gold, in the Predynastic period, *i.e.* before King Narmer (about 3500 B.C.). The early iron was very scarce and was perhaps obtained from meteorites which originally fell upon the earth from outer space, or the natural metal itself. This Predynastic iron was used as beads for jewellery, strung with beads of lapis lazuli, and a necklace of this kind was found in a very early tomb by Petrie. Iron tools occur in the pyramid



of Cheops (2500 B.C.) and the metal was plentiful in Egypt about 2000 B.C. This iron seems to have come from the Land of the Hittites, in Asia Minor, around the Black Sea. The Hittites

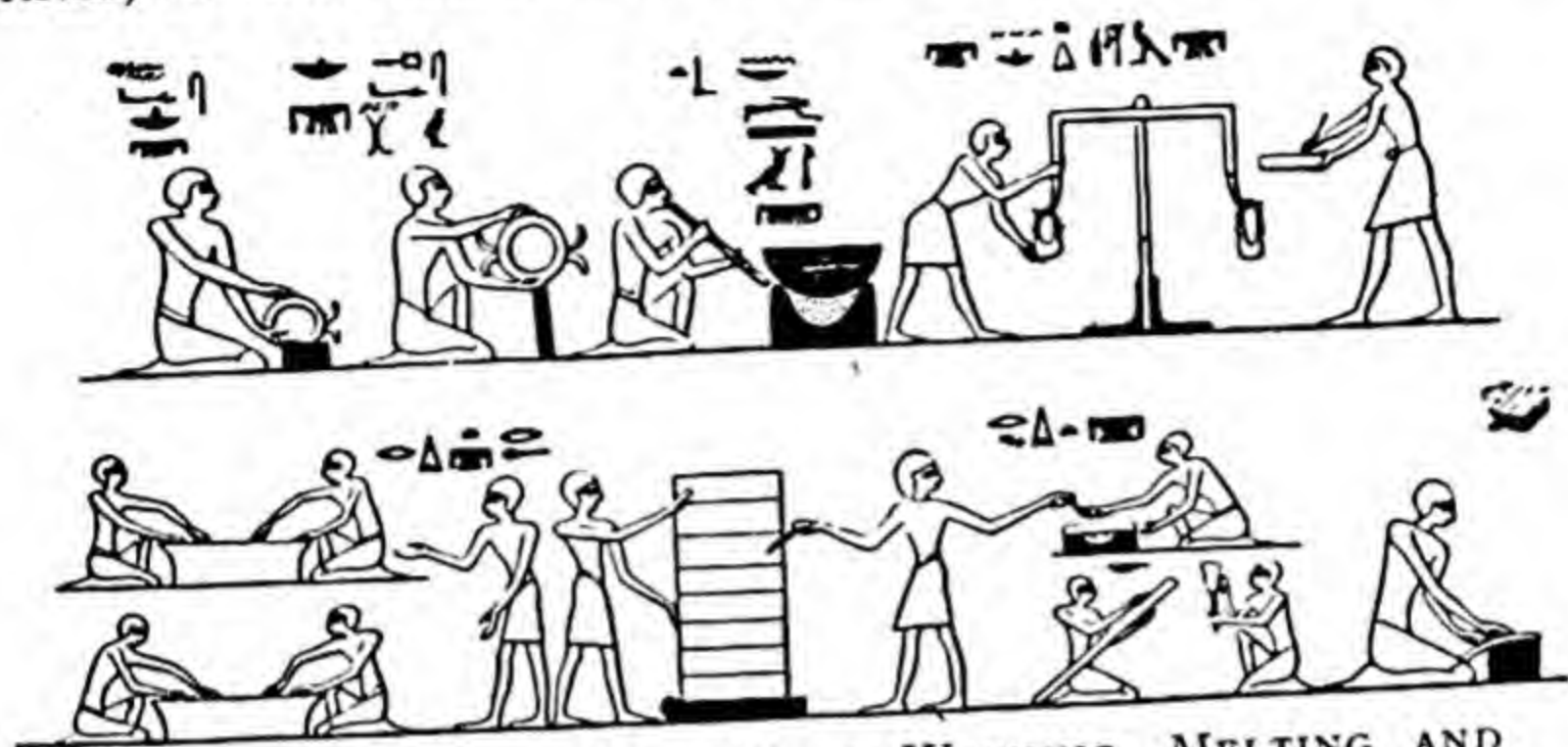


FIG. 20.—EGYPTIAN GOLDSMITHS WASHING, MELTING AND WEIGHING GOLD.  
BENI HASSAN, 1900 B.C.

were skilled in making iron, and an original letter has been found written by a king of Egypt to the king of the Hittites asking for a supply of iron, and another from the king of the

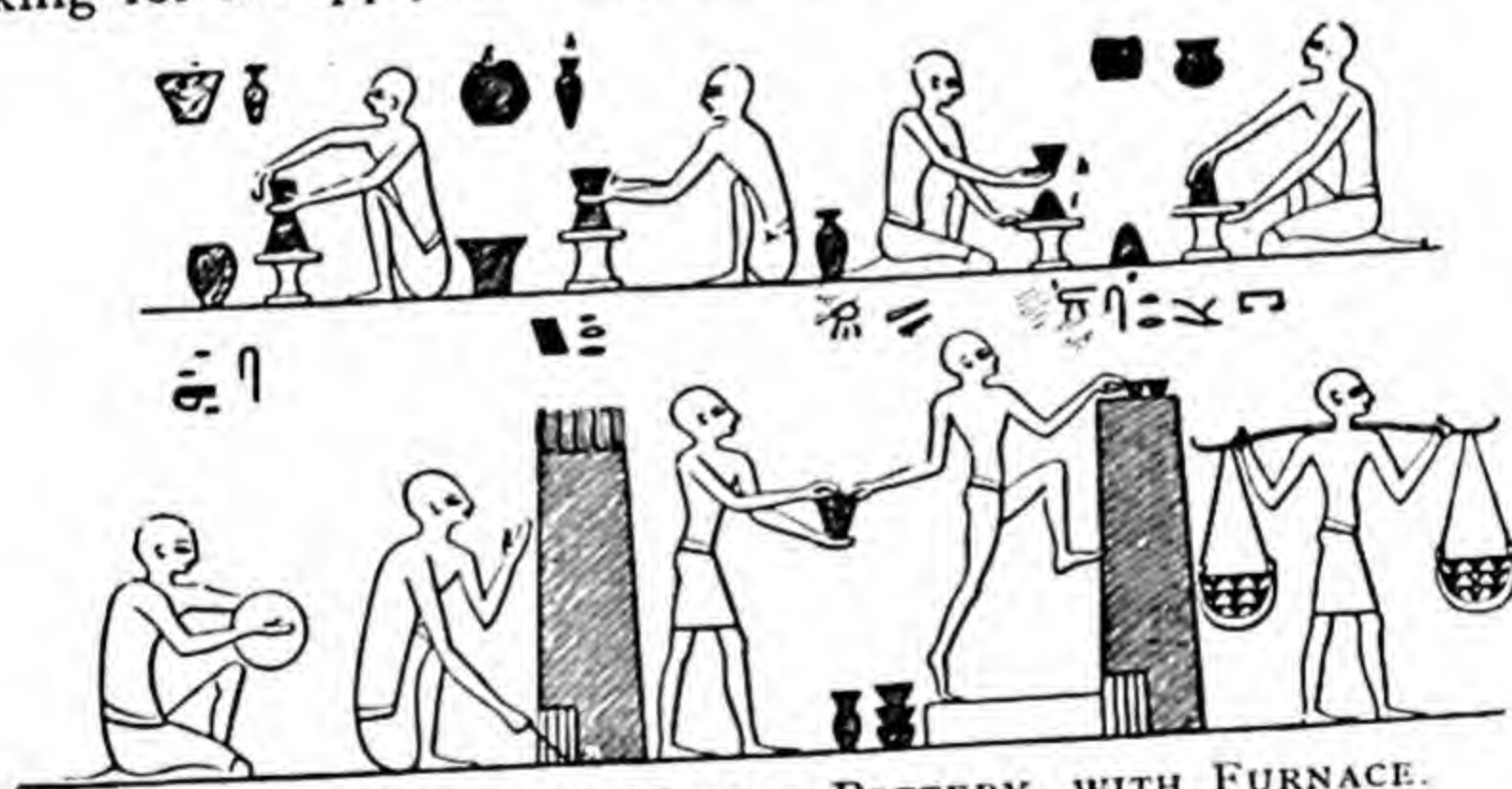


FIG. 21.—EGYPTIANS MAKING POTTERY, WITH FURNACE.  
BENI HASSAN, 1900 B.C.

Hittites in reply, asking for gold in exchange, 'which in my brother's land is as common as dust'!

The metal *orichalcum* mentioned by Plato (B.C. 400) as known but forgotten long before his day, may have been *brass*. Brass

was well known in the Roman period : coins of it (25 A.D.) have been found. A passage in Strabo, about the beginning of the Christian era, has been thought to describe the production of metallic zinc, and small figures consisting largely of zinc and dated to about the time of Strabo have been found in Europe. Early Chinese bronzes contain considerable amounts of zinc, and this metal seems to have been known in the Far East at an early date.

**Glass.**—Side by side with the working of metals, the Egyptians and the inhabitants of Mesopotamia perfected the arts of making



FIG. 22.—PREDYNASTIC EGYPTIAN POTTERY, WITH FIGURE OF BOAT(?). BEFORE 3400 B.C. (British Museum.)



FIG. 23.—GLAZED FAIENCE FIGURE : EGYPT, FIRST DYNASTY, 3400 B.C. (British Museum.)

glazed pottery or other similar materials, and the production of glass. The Egyptian potter very soon learnt the use of the wheel for moulding the clay, and the vessels were baked in tall closed furnaces, not in open fires (Fig. 21). The very earliest pottery is unglazed and has a buff-coloured decoration (Fig. 22).

Blue and green opaque glazes containing copper compounds were used at a very early period in Egypt (Fig. 23). Recently, pale green true glass beads belonging to the Predynastic period (before 3400 B.C.) have been found by Petrie at Naqada. A blue glass vase (Fig. 24) of Thothmes III (1550 B.C.) and some other early Egyptian glass is in the British Museum. The



manufacture of glass on the large scale apparently began in Egypt about 1370 B.C.; in the remains of a glass factory of this period at Tell el-Amarna, excavated by Petrie, nearly the whole process came to light. The alkali (*natron*, sodium carbonate found in Egyptian lakes near Alexandria, and incorrectly translated 'nitre' in the English Bible) was melted with crushed quartz, limestone, and copper compounds in crucibles to form a blue glass. Nearly colourless glass was also made at an early date in Egypt.

Egyptian glass making was developed especially at Alexandria, a city founded at the head of the Nile Delta by Alexander the Great in 331 B.C. Glass made there was exported to all parts of the Roman Empire, although in some places there were native glass factories, *e.g.* in Syria, and probably also in Britain, where remains of glass furnaces of the Roman period have been found near Warrington. Glass making was also developed by the Assyrians; a glass bottle of King Sargon (700 B.C.) in the British Museum, formerly thought to be of Egyptian manufacture, is probably an Assyrian product, since there is inde-

pendent evidence that the manufacture of coloured glass was highly developed in that country about this time. A blue glass called *uknu* is described as an imitation of lapis lazuli in Assyrian tablets in the British Museum, dated about 650 B.C.

The chemist has taught the modern manufacturer to make many new and useful kinds of glass. Common glass containing soda, lime and silica (sand), cracks easily when suddenly heated or cooled, and if strongly heated it softens and vessels made from it become distorted. By adding boron compounds, and some metallic oxides in place of some constituents of ordinary glass, **Jena glass** was produced which resists high temperatures and is useful for chemical apparatus. More recently American and British chemists have produced **Pyrex glass** and similar varieties.

Pyrex glass is strong and stands temperature changes so well that tea-pots and cooking dishes can be made from it (Fig. 25).



FIG. 24.—TURQUOISE-BLUE OPAQUE GLASS VASE OF THOTHMES III, EGYPT, 1550 B.C.

(British Museum.)

Finally, even silica itself can be made into a transparent or into a kind of opaque glass called *silica glass* or *vitreous silica*, which has such a small coefficient of expansion that it may be heated to redness and plunged into cold water without fracture (see p. 471). Pliny and other Roman authors mention a malleable glass, a vessel of which was shown to Nero by the inventor. The

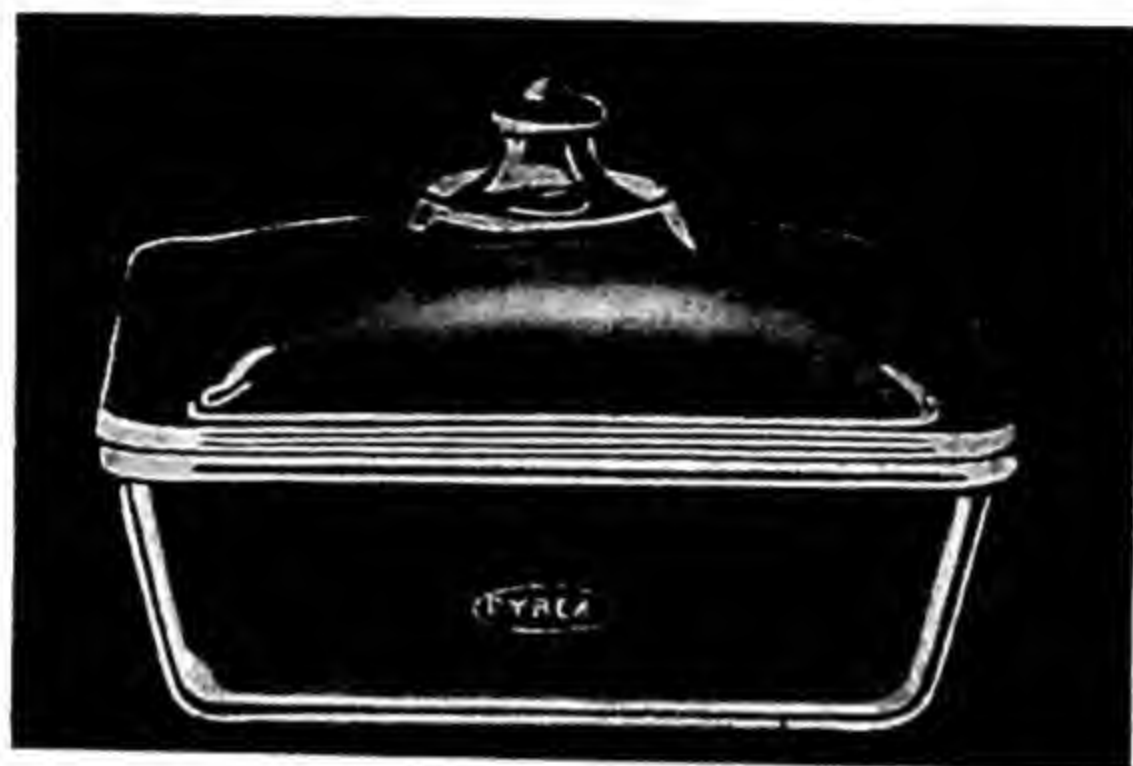


FIG. 15. PYRAL GLASSWARE.

Emperor asked the artisan if anyone else knew his secret, and when he was told no, he ordered the unfortunate man to be put to death, since his knowledge was likely to be dangerous. We do not know what the material was. The celebrated *vasa aurea* in the 14th century are thought to have been coloured glass, and no certain examples of this type are known. In the 16th century glass was very cheap.

Agriculture, chemistry, engineering, science. New chemical discoveries are made every day and new conditions are constantly



being set the chemist by the needs of advancing civilisation. Natural sources are being exhausted: coal and oil will not last for ever, and the utmost skill of the chemist will be required if mankind is not to return to the conditions of the savage state.

An even worse fate might have been in store for man but for the resources of chemistry. The growing of wheat requires fertilisers to be supplied to the soil, which otherwise becomes sterile and unfit for the production of crops. It is said that vast areas of land in America have been put out of use in this way.

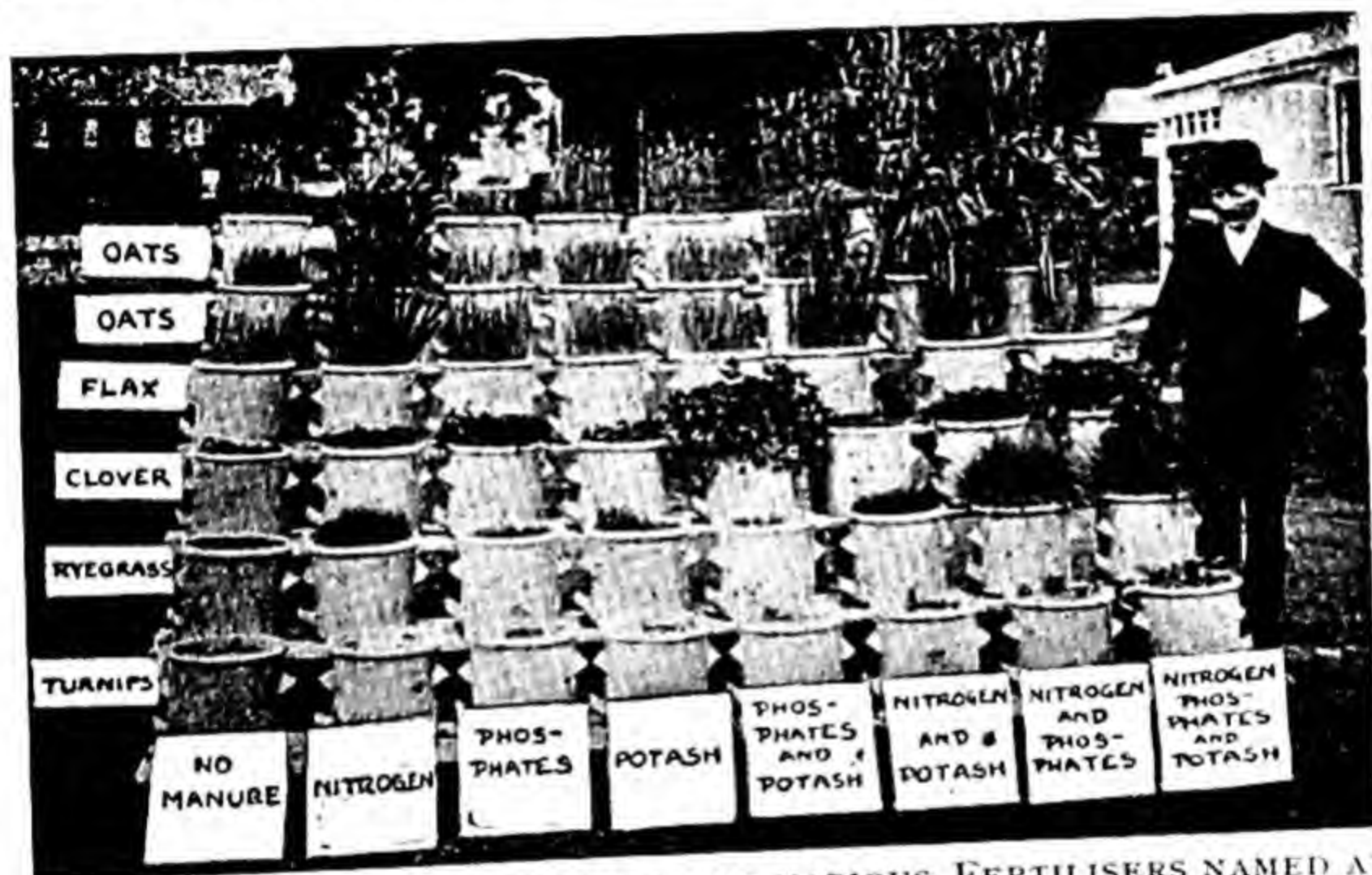


FIG. 26.—THE EFFECTS OF SUPPLYING VARIOUS FERTILISERS NAMED AT THE FOOT OF THE ILLUSTRATION TO VARIOUS CROPS NAMED ON THE LEFT.

THE PLANTS HAVE BEEN GROWN FOR THE SAME LENGTH OF TIME UNDER OTHERWISE EQUAL CONDITIONS.

Although the Romans paid great attention to the subject, agriculture was really declining until the functions of fertilisers became understood about 1840 A.D. In England the production of wheat has increased from six to thirty-two bushels per acre in the last seven hundred years, a part of the increase being due to the use of fertilisers. Belgium and Germany produced in 1913 an average of thirty-five bushels per acre, and used more fertilisers than England.

The soil is naturally enriched by the growth of leguminous plants such as clover, peas and beans, and it was known many centuries ago that the yield of grain could be increased if a crop

of leguminous plants had been grown on a field the year before. The principle of crop rotation, discovered empirically or by rule of thumb, has a scientific basis, since the leguminous plants are associated with bacteria which can turn the free nitrogen of the air into compounds which act as fertilisers (*see* p. 369).

The natural sodium nitrate found in the nitrate beds in Chile is within sight of exhaustion, and the late Sir William Crookes pointed out that unless some artificial source of nitrates (or other suitable nitrogen compounds) could be found, those parts of the human race which depend largely on bread would in years to come be faced with starvation. Even as Crookes was speaking, chemists were at work on the problem, and there are now several processes in operation on the large scale for making nitrogen compounds from the air, which provide an abundant and assured supply for the purposes of agriculture, and make us independent of the Chilean deposits.

The production and use of fertilisers and insecticides, the examination of soils and the correction of the injurious properties of certain materials, all form part of the application of chemistry to agriculture. A king of Carthage, Juba, is said by Pliny to have written books on agriculture, and in the Roman period the great landowners were especially interested in the subject. It then relapsed into a state of empiricism, and was considered somewhat beneath the dignity of scientific study. Early in the nineteenth century, Davy, the most eminent chemist of the time, turned his attention to it. He was followed by Liebig and others, and since then chemistry has proved of the greatest value to the farmer.

**Chemistry and the community.**—We might go on to tell of other ways in which chemistry has contributed to improve and ameliorate the life of man; of pottery and porcelain, tanning, the manufacture of soap, paper, perfumes, and the like, but enough has been said to show how very essential it is that the study of chemistry should go on, so that new discoveries may be made and new applications of old discoveries found.

It is a mistake to suppose that chemists always set out to make discoveries which shall have an immediate application to definite technical problems. This is no doubt sometimes the case, as in the production of new dyestuffs, but many important applications of chemistry arose from quiet work in the laboratory without thought of technical value. The pursuit of the science for the sake of advancing knowledge has absorbed the lives of many famous chemists. The mechanical and chemical manu-



facturer has rarely discovered anything,' said Davy in 1829, 'he has merely applied what the philosopher has made known, he has merely worked upon the materials furnished to him.' It is not asserted that the transition from the laboratory experiments to the industrial plants or installations, by which alone the discoveries of science can be made of service to the community, does not involve the application of great skill and patience and often the expenditure of large sums of money, but without the preliminary efforts of scientific discoverers, these qualities would generally have nothing to work upon and little or no progress could be made. Big business usually arises from a little exhibition of genius in another place, and very often the scientific investigator who has made possible great and lucrative industrial undertakings has died in poverty.

In some cases the results of improper exploitation of scientific discoveries have been harmful: the adulteration of foods, and the fraudulent replacement of more expensive materials by inferior imitations which the advance of chemistry has made possible, call for constant vigilance and control by skilled chemists. Most of the large industries employ chemists to test the purity of the materials they buy and the products they sell—the latter partly because these products are in turn subjected to rigorous examination by the purchasers' chemists or by analysts in the public service.

The applications of chemistry in the detection of crime are well known to readers of fiction, and the examination of documents for forgery calls for the use of chemical methods.

Apart from its direct uses in life, chemistry has an important educative value. Very few of the students of science become chemists, yet the study of the subject is also a study in scientific method which cannot fail to be valuable in other walks of life. The central feature of scientific method is *appeal to experiment*: 'try it' is the guiding principle. The applications of scientific method in business life—the correlation of facts, the way of thinking in terms of ascertained realities, the receptivity for new ideas and new results, and the habit of facing difficulties in a straightforward manner, in realising that mistakes have been made and their rectification before it is too late, all these are features which are well emphasised in a scientific training. In an experimental science the sharpening of the powers of observation is of the first importance. ~~Everything~~ which can be learnt from an experiment should be noticed and no detail should be lost sight of. In the preparation of a gas, for example, it is not

sufficient merely to put the materials together and collect the gas—every change which occurs, alterations of colour, the rapidity with which the change takes place, any products which are not the one intended, all these are important and must be seen by the manipulator. A chemist has a genuine interest in the materials he uses. It has been said that every one of the numerous white precipitates known to the chemist has some quality or qualities peculiar to itself which should be recognised by those who have once fully studied it, and the chemist Liebig was able to recognise substances by their appearance alone with such certainty that he was not even misled by the results of the analysis of impure specimens.

Chemistry forms part of that great collection of studies of Nature which we call Science: its pursuit is associated with other sciences in many ways. The Chemist must know something of Physics and the Botanist something of Chemistry. As time goes on, the boundaries between the separate sciences become indistinct and it is seen that the study of Nature cannot be marked off into sharply defined regions. In this book we shall have to deal briefly with some subjects, such as the properties of gases and electrolysis, which could equally well go into a course in Physics. Yet they are closely related to Chemistry and we could not understand the latter fully without them.



## CHAPTER II

### PURE SUBSTANCES, MIXTURES, AND SOLUTIONS

**Different kinds of solids, liquids and gases.**—In the chemical laboratory we find a large number of substances, some labelled



FIG. 27.

ILLUSTRATING THE DIFFERENT DENSITIES OF SOLIDS AND LIQUIDS.  
EQUAL WEIGHTS OF THE SOLIDS AND EQUAL WEIGHTS OF THE LIQUIDS  
ARE CONTAINED IN THE BOTTLES.

'pure,' others 'commercial,' *i.e.* sufficiently pure for many purposes but not for accurate chemical work. There will be

bottles containing white and coloured crystals and powders and various kinds of liquids. There are also steel cylinders containing compressed gases, such as oxygen and hydrogen. Among the things with which a student of chemistry must learn

to become familiar are the appearance and uses of common laboratory substances and apparatus. Every material used in practical chemistry should be carefully examined: its colour, crystalline form and density (Fig. 27) (*i.e.* whether it is heavy or light, as judged by the weight of the bottle containing it) should all be noticed.



FIG. 28.—CALCITE, SHOWING CONCHOIDAL FRACTURE AND CRYSTALLINE FRACTURE OR CLEAVAGE IN THE SAME MATERIAL. (After Miers.)

Substances which do not crystallise are called **amorphous**: powdered charcoal, magnesium oxide, and some kinds of manganese dioxide are amorphous powders, and glass is an amorphous solid. Some powders are really composed of very small crystals, which may often be recognised under a lens or a microscope. A mass of a crystalline substance usually breaks with a **crystalline fracture**, an amorphous with a **conchoidal fracture**, *i.e.* one like the inside of a shell (Fig. 28).

**Homogeneous and heterogeneous bodies.**—A characteristic of a pure substance is that all parts of it are chemically exactly alike. All pieces of copper sulphate crystals (Fig. 43), although they may be of very different sizes and appear of different accidental shapes owing to fracture, are obviously composed of one material only. We say that such things are

**homogeneous bodies**, meaning that the body has the same properties in all its parts. A piece of clear Iceland spar (or calcite) (Fig. 28) is homogeneous. A piece of granite is, on the other hand,



FIG. 29.—SECTION OF GRANITE, SHOWING THAT IT IS A HETEROGENEOUS MATERIAL.



perceived by inspection to consist of an aggregate of three different minerals (Fig. 29). One is pink or grey, opaque, and capable (though with difficulty) of being scratched with a knife; it is felspar. A second is colourless, transparent, and too hard to scratch with a knife; this is quartz. The remaining mineral is in the form of thin grey, or black, plates, which can be split by a knife into very thin leaves; it is mica.

Bodies such as granite, which show different properties in different parts of the mass, are called **heterogeneous bodies**, or sometimes the older name **mechanical mixtures** is used to describe them.

**The purification of materials.**—Since chemistry is primarily concerned with the study of pure substances, heterogeneous bodies must first be separated into their components. The same



FIG. 30.—EGYPTIAN GOLD WASHING.  
THE WATER IS BEING SQUEEZED OUT IN A KIND OF BAG.

is generally true in technical processes. For example, the ores of most metals are accompanied by useless rocks, and before the ore is smelted, as much of the inert rock is removed as possible. The methods used in the separation of mechanical mixtures include **hand-picking** when the material is coarse-grained; **magnetism** when one of the materials is attracted by a magnet and the others not; and **sedimentation** when one constituent (e.g., metallic ore) is heavier than the other (e.g., rock). When the mixed powder is stirred up with water, the heavier part can be allowed to sink while the lighter is washed away; this method has been used from very early times in 'washing' gold from sand and in Egyptian inscriptions we find it represented along with the name (composed of the signs for *water* and *gold*) 'river gold' (Fig. 30). Finally, we can effect separation by **dissolving** out one constituent and leaving the others, as when sugar is dissolved from admixture with sand by means of water. In the last case, **filtration** will separate the solution from the residue.

**The separation of solids and liquids by filtration.**—In the laboratory, filtration is usually carried out by allowing the liquid

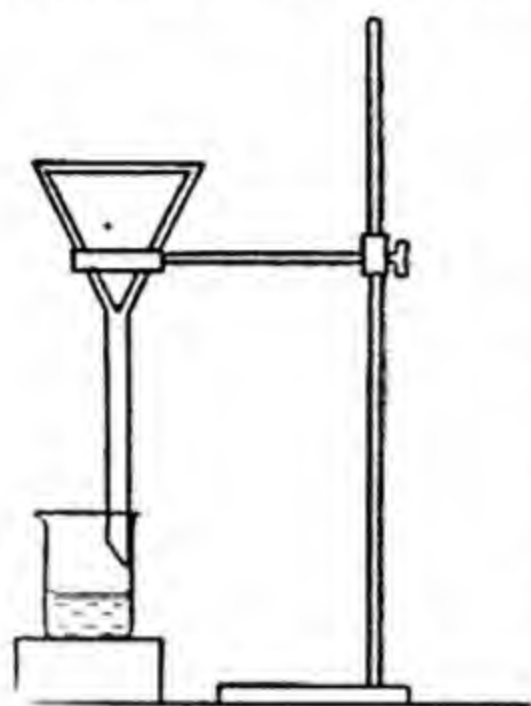


FIG. 31.—APPARATUS FOR FILTRATION.

to flow through a circular piece of **filter paper** (a porous unglazed paper) folded into a cone and supported in a glass funnel (Fig. 31), but on the large scale cloth is often used and the liquid forced through under pressure by pumps in a **filter press**. The liquid passes through the pores of the paper or cloth and the suspended solid particles, which are generally too large to pass through the pores, are held back. In the laboratory the rate of filtration may be hastened by withdrawing with a filter pump part of the air from a closed flask into which the funnel with a

perforated disc is fitted (Fig. 32). The atmospheric pressure acting on the surface of the liquid in the funnel drives it through the filter paper which is laid on the perforated disc.

On the large scale, **vacuum filters** acting on the same principle are used, but the paper is then replaced by a **filtering cloth**, usually stretched over a perforated drum which dips into a bath of the liquid to be filtered and is caused to rotate. The pressure of the air inside the drum is reduced. The solid deposited on the outside of the cloth is scraped off continuously by a scraper in contact with the drum. The Hele-Shaw stream-line filter consists of a column of circular discs of paper, pressed together, and the liquid is forced through from the outside by pressure or suction. The clear liquid passes off through a channel through the centre of the pile of discs. This apparatus has been used in separating fine dirt from lubricating oil which has been used in motor engines,

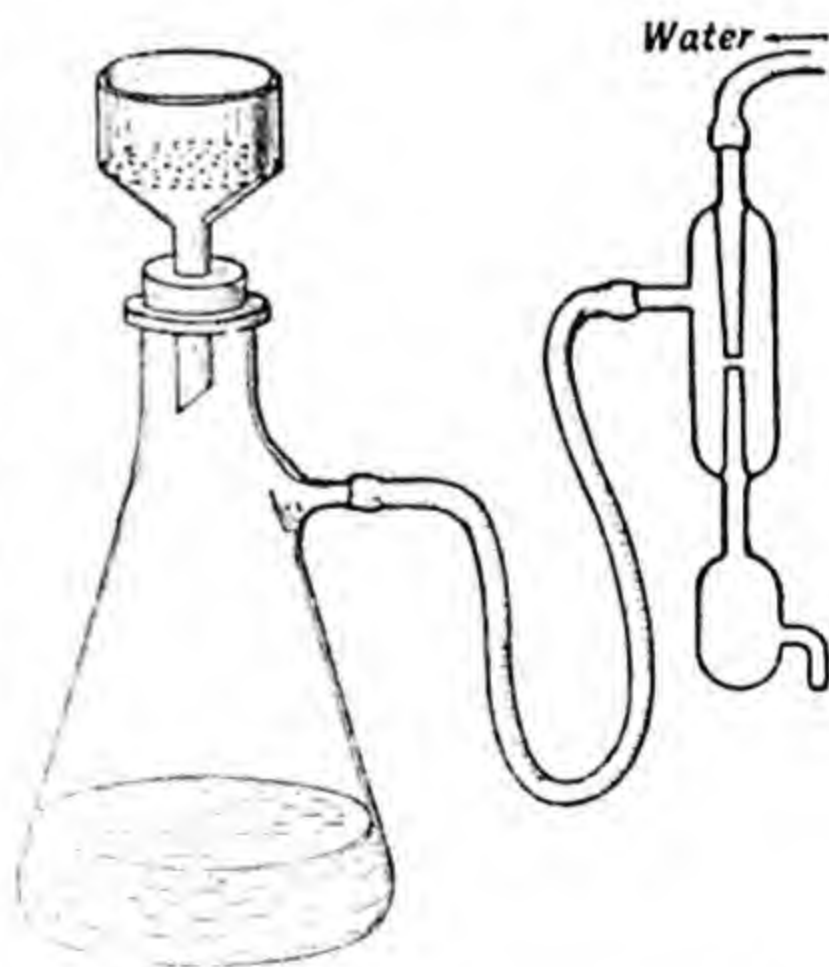


FIG. 32.—FILTRATION UNDER REDUCED PRESSURE.



in separating oil from water on board ship, and for other purposes.

**Solutions.**—A common laboratory operation is the separation of the constituents of what are called solutions. It is known



FIG. 33.—STREAM LINE FILTER.



FIG. 33A.—SECTION OF FILTER WITH ACCUMULATED RESIDUE.

from everyday experience that water is capable of *dissolving* solids, such as sugar in a cup of tea, or salt, to form solutions (Fig. 34). These solutions contain the dissolved substance, or *solute*, as it is sometimes called, in an extremely finely divided form, uniformly distributed through the liquid and with no tendency whatever to settle out on standing.

Water is a useful *solvent*, *i.e.* a substance (generally liquid) which dissolves other substances. There are many things which are *insoluble* in water: *e.g.* oil, wax, indigo. Oil and grease are easily soluble in benzine or petrol, which are used in dry-cleaning soiled clothes. Varnish is a solution of certain resins in alcohol, linseed oil, or other solvents, and on application the alcohol evaporates or the oil hardens and leaves a transparent film impervious to water. the new cellulose finish for motors, contain products of cellulose (the principal constituent of cotton-wool or paper) called nitro-cellulose or acetyl cellulose, in a mixture of solvents containing

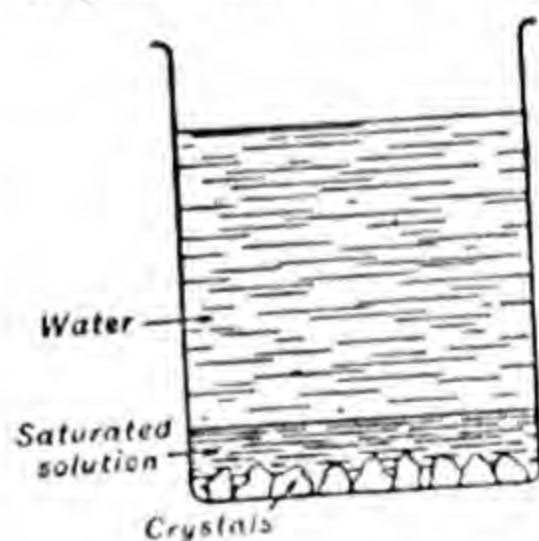


FIG. 34.—A SOLID PASSING INTO SOLUTION IN A LIQUID.

Aeroplane 'dope,' and

acetone and amyl acetate, a liquid smelling very strongly of pear drops.

Some of the new 'cellulose lacquers' contain chemicals which a few years ago were hardly known. Their valuable properties have been discovered by trial and now that they are required these solvents can be made cheaply and in large quantities. Substitutes for resins can also be made.

Solutions in alcohol are called *tinctures* or *spirits*, e.g., tincture of iodine ; spirit of camphor.

True solutions are homogeneous (p. 28), and the dissolved substance is in an extremely fine state of subdivision. Thus, 1 gm. of the red dye eosin gives a distinct fluorescence to 1,000,000 c.c. of water when examined in a strong light. Each cubic centimetre of the solution contains only 0.000,001 gm. of the dye, and since a volume of only  $10^{-12}$  c.c. of solution can be examined under the microscope, this can contain only  $10^{-18}$  gm., or 0.000,000,000,000,000,001 gm. of dye.

This dye is sometimes used to detect the communication of water supplies underground.

**Distillation.**—Dissolved solids are separated from liquids by distillation. A simple apparatus for distillation consists of a

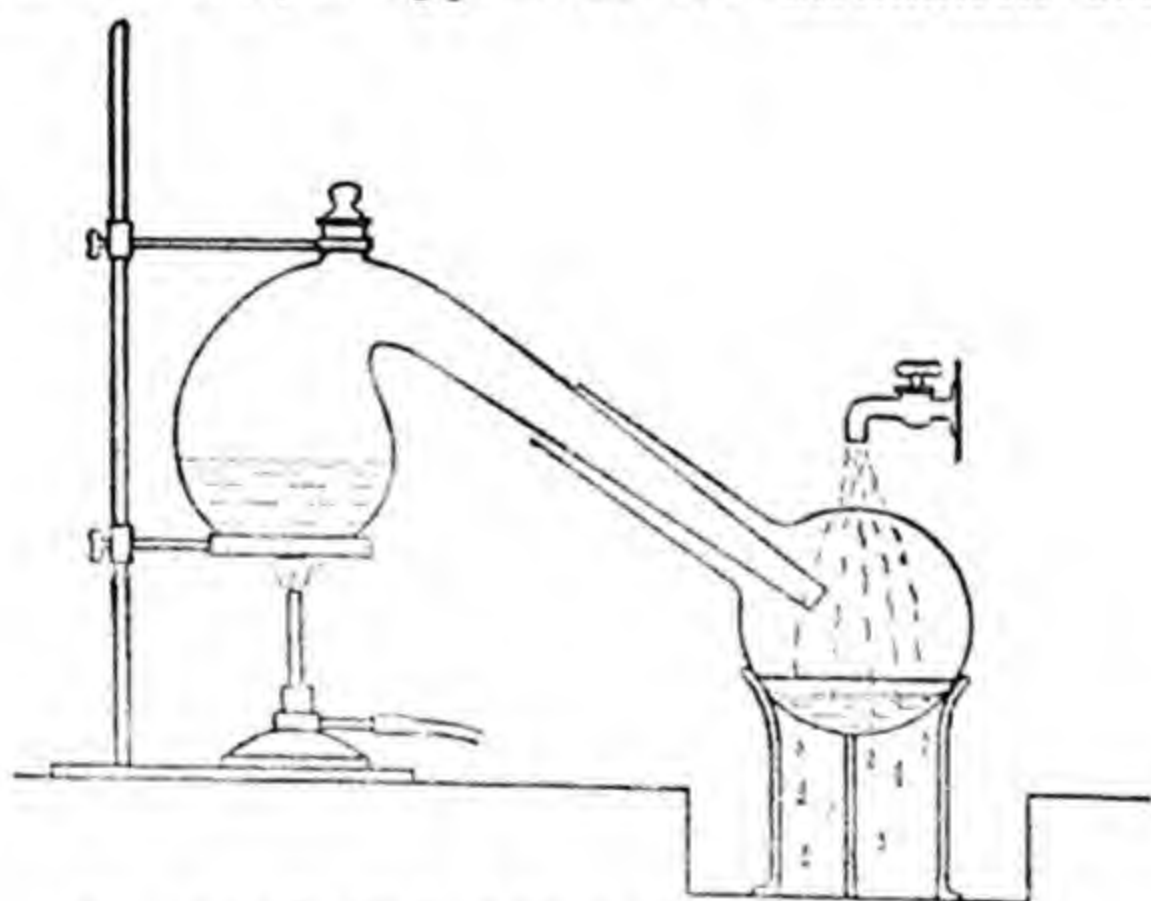


FIG. 35.—SIMPLE APPARATUS FOR DISTILLATION,  
CONSISTING OF A RETORT AND RECEIVER.

glass retort with the neck passing into a glass flask, or receiver, which is cooled by water (Fig. 35). The dissolved solid (e.g. salt in sea water) remains behind in the retort.

If larger quantities of liquid are to be distilled it is more



convenient to use a Liebig's condenser (Fig. 36), consisting of a glass tube enclosed in a jacket through which a constant stream of cold water is passed. A thermometer may be fitted through the cork of the flask, with the bulb suspended in the vapour coming from the boiling liquid. With this apparatus it is possible to separate not only solutions of solids in liquids, but also, at least partially, solutions of liquids in liquids. Thus, if a mixture of equal volumes of alcohol (b. pt.  $78.3^{\circ}$ )\* and water (b. pt.  $100^{\circ}$ ) is distilled, it is found that the boiling point at the commencement of the operation is  $84^{\circ}$ . The liquid collecting in the

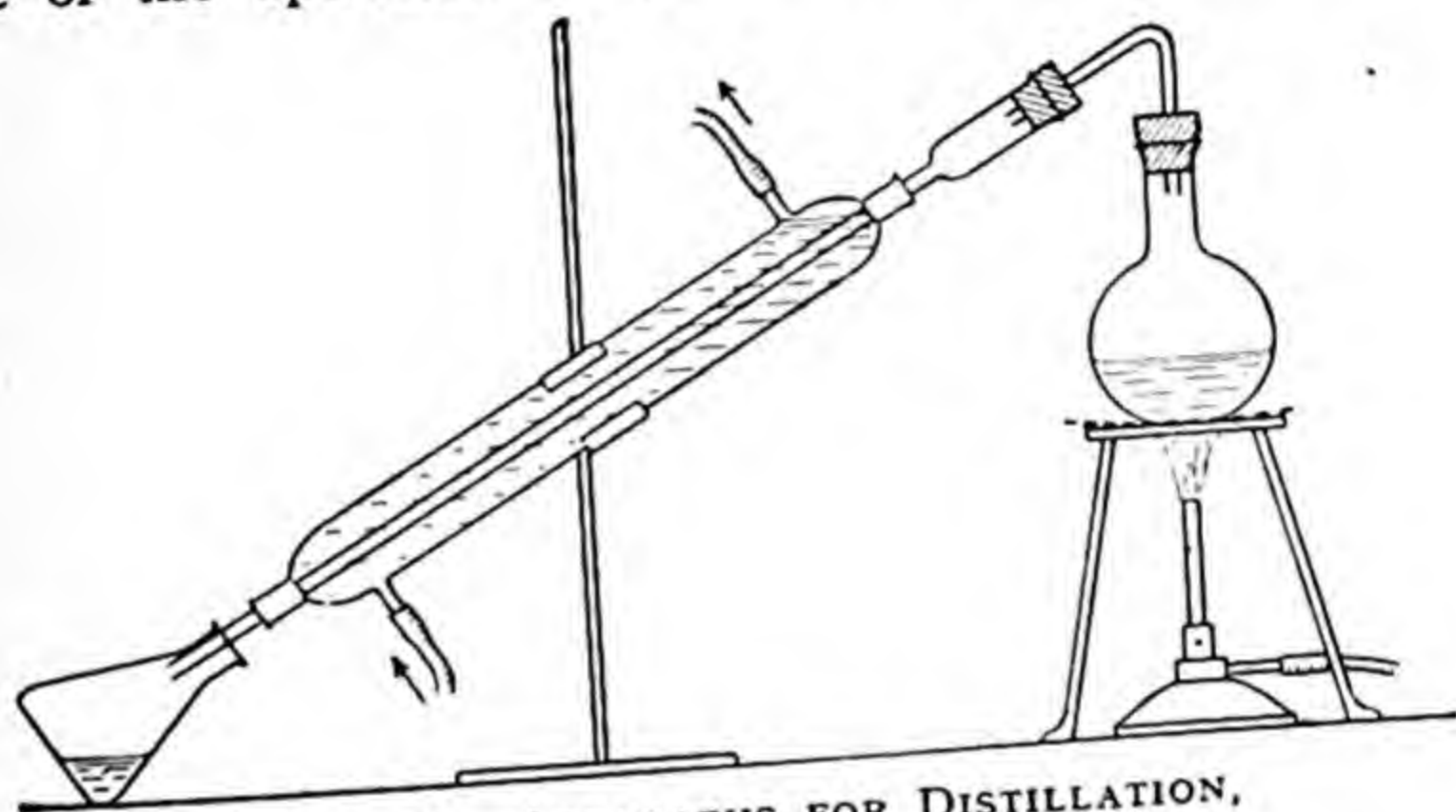


FIG. 36.—APPARATUS FOR DISTILLATION,  
WITH LIEBIG'S CONDENSER.

receiver is richer in alcohol than the original mixture, and will burn when lighted in a dish. As the distillation proceeds, the boiling point rises, and the distillate contains more and more water. If the distillation is stopped when one-fourth of the mixture has distilled over, and the boiling point has risen to  $85.5^{\circ}$ , it will be found, if the distillate is poured into a clean flask and the operation repeated, that it begins to boil at  $81.5^{\circ}$ , *i.e.*, at a lower temperature than the original mixture, and the first portion of the distillate is correspondingly richer in alcohol. This partial separation of liquids is called **fractional distillation** and is used on the large scale (Chapter XXVII).

**Solutions of liquids in liquids.**—Some liquids, such as water and mercury, are practically immiscible; others, such as water and alcohol, are completely miscible. In some cases, such as ether and water, each liquid dissolves a limited amount of the

\* All temperatures in this book are in degrees Centigrade.

other, and the liquids are **partially miscible**. If successive *small* quantities of ether are added to water, they at first dissolve completely, but a point is reached when no more ether will dissolve and two liquid layers are formed. These may be separated in



FIG. 37.  
SEPARATING  
FUNNEL.

a **separating funnel** (Fig. 37); the presence of ether in the lower aqueous layer may be shown by heating it in a test-tube, when the ether vapour given off may be kindled. The presence of water in the upper ether layer may be shown by dropping a bit of the metal sodium into it when an inflammable gas, hydrogen, is evolved. Pure ether has no action on sodium.

If to the two layers of ether and water a little iodine is added, which dissolves in each solvent, it is found on shaking that the iodine is shared between the two liquids, but most of it, as is seen from the darker brown colour of the solution, is taken by the ether.

Ether may therefore be used for the **extraction** of iodine from a solution in water. Chloroform and carbon disulphide also extract iodine, the solutions in this case being violet in colour. This is made use of in testing for iodine. The method is used for the extraction of many other substances from their solutions in water.

**Solutions of gases in liquids.**—It is easy to prove by experiment that *liquids can dissolve gases*. A flask and delivery tube are completely filled with rain water or tap water, and the flask is heated: bubbles of gas appear, which pass out of the delivery tube under water (Fig. 38), and will be found to be mainly air; such water therefore contains *dissolved gas*. The solubility of a gas increases with pressure: when a bottle of soda-water is opened the dissolved gas escapes in bubbles owing to the reduction of pressure. The solubility of a gas decreases with rise in temperature, as the experiment described above shows. Dissolved gas is

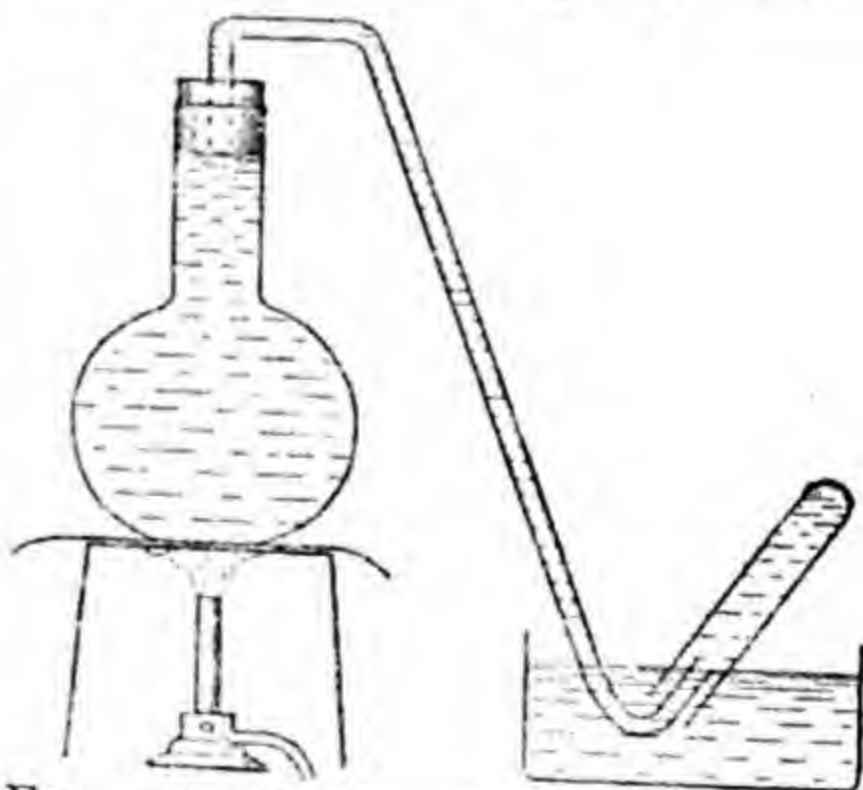


FIG. 38.—SEPARATING DISSOLVED  
AIR FROM WATER BY HEAT.



sometimes removed from water to be used in steam boilers by preliminary heating, to reduce corrosion of the boiler.

Even *solids* are capable of dissolving gases; for example, the rare metal palladium will dissolve about 600 times its bulk of hydrogen, and solids may also dissolve other solids. Thus, if a piece of gold-leaf is pressed on a freshly-scraped piece of lead, the gold slowly penetrates, or *diffuses*, into the latter. It is thought that the green colour of emeralds, or the red colour of rubies, is due to small quantities of dissolved substances.

**Solutions of solids in liquids.**—The most important solutions are formed by dissolving solids in liquids. Common salt added in successive small amounts to water dissolves up to a certain point; after this salt no longer passes into solution, but settles out unchanged. The salt will dissolve more rapidly when the mixture is stirred, since then diffusion, or the spreading of the dissolved substance so as to distribute itself uniformly, takes place more easily. When a solution can exist unchanged in contact with the solid which is partly in solution, it is said to be *saturated*. A solution which will dissolve more solid when brought in contact with it is called *unsaturated*. It may become saturated when stirred up with excess of solid, and more rapidly when the solid is powdered (Fig. 34).

Since a saturated solution can remain unchanged in contact with solid, it is said to be in *equilibrium* with the solid. Equilibrium is a state of balance. We are familiar with the idea of equilibrium in physics (*e.g.* see Hadley, *Everyday Physics*, p. 25), and we shall find that it is also very important in chemistry.

We must be very careful not to say that a 'saturated solution is one which has dissolved as much solid as possible.' It is easy to show by experiment that this is incorrect. A large test-tube is half filled with crystals of sodium thiosulphate ('hypo'), and the neck plugged with cotton wool. The tube is then heated in a beaker of boiling water. The salt

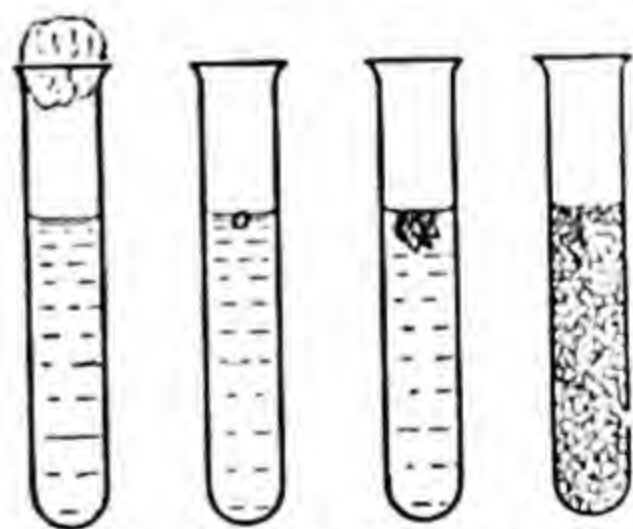


FIG. 39.—CRYSTALLISATION OF A SUPERSATURATED SOLUTION.

melts in its own water of crystallisation (p. 39), and forms a very concentrated solution. On cooling, this remains liquid; it is then a *supersaturated* solution. On removing the plug and dropping into the liquid a crystal of hypo, the liquid at once begins to solidify, and the mass becomes

warm, since heat is evolved in the process. Supersaturated solutions invariably crystallise in contact with the solid form of the solute. The crystallisation is seen to spread from the crystal of solid dropped in (Fig. 39).

**Equilibrium in saturated solutions.**—Since equilibrium is a state of balance, when two opposing tendencies just neutralise each other, we may suppose that the tendency of solid to go into solution is just balanced, in a saturated solution, by the tendency of the dissolved solid to come out of solution, or to crystallise. When a saturated solution is in contact with the solid, although the whole seems to be unchanged, yet solid is actually passing into solution, and solid crystallising out from solution, at the same time, and the two changes go on at exactly the same rate. This can be demonstrated experimentally, since if crystals are immersed in saturated solutions they often change, so that broken or imperfect parts become

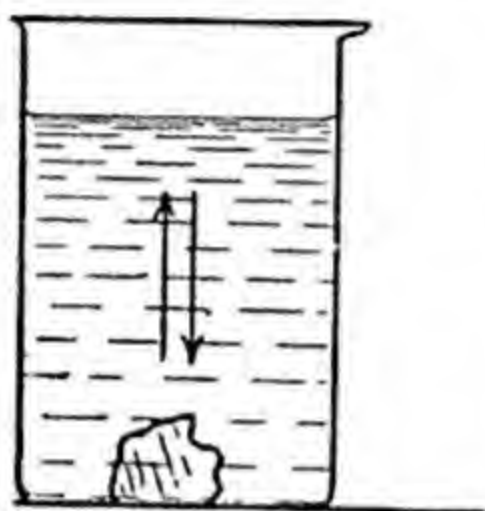
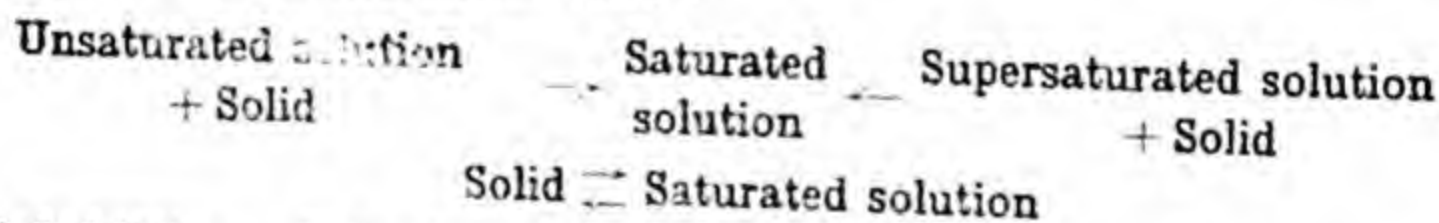


FIG. 40.—EQUILIBRIUM BETWEEN A SOLID AND A SATURATED SOLUTION.

perfect, although the whole crystal has the same weight as before. In unsaturated solutions the rate at which the solid substance dissolves is greater than the rate at which the dissolved substance deposits. In supersaturated solutions the opposite is true. Contact with the solid salt ultimately brings both types of solution into the equilibrium state of a saturated solution.

The state of equilibrium is usually denoted by the symbol  $\rightleftharpoons$ , or  $\rightleftharpoons$ , which indicates that two opposite changes,  $\rightarrow$  and  $\leftarrow$ , are taking place at the same rate :



**Solubility.**—Solutions are commonly called 'strong' or 'weak' according as they contain more or less dissolved substance. A more scientific way of stating this is to give what is called the concentration of the solution, which is the number of grams of dissolved substance associated with 100 grams of the solvent. The concentration of a saturated solution of a solid is called the solubility of the latter: it is the number of grams of solid dissolved by 100 grams of solvent at a given temperature in presence of excess of solid. For example, the solubility of



common salt in water is 35.9 at  $15^{\circ}$ , since 100 grams of water at this temperature are saturated by 35.9 grams of the salt.

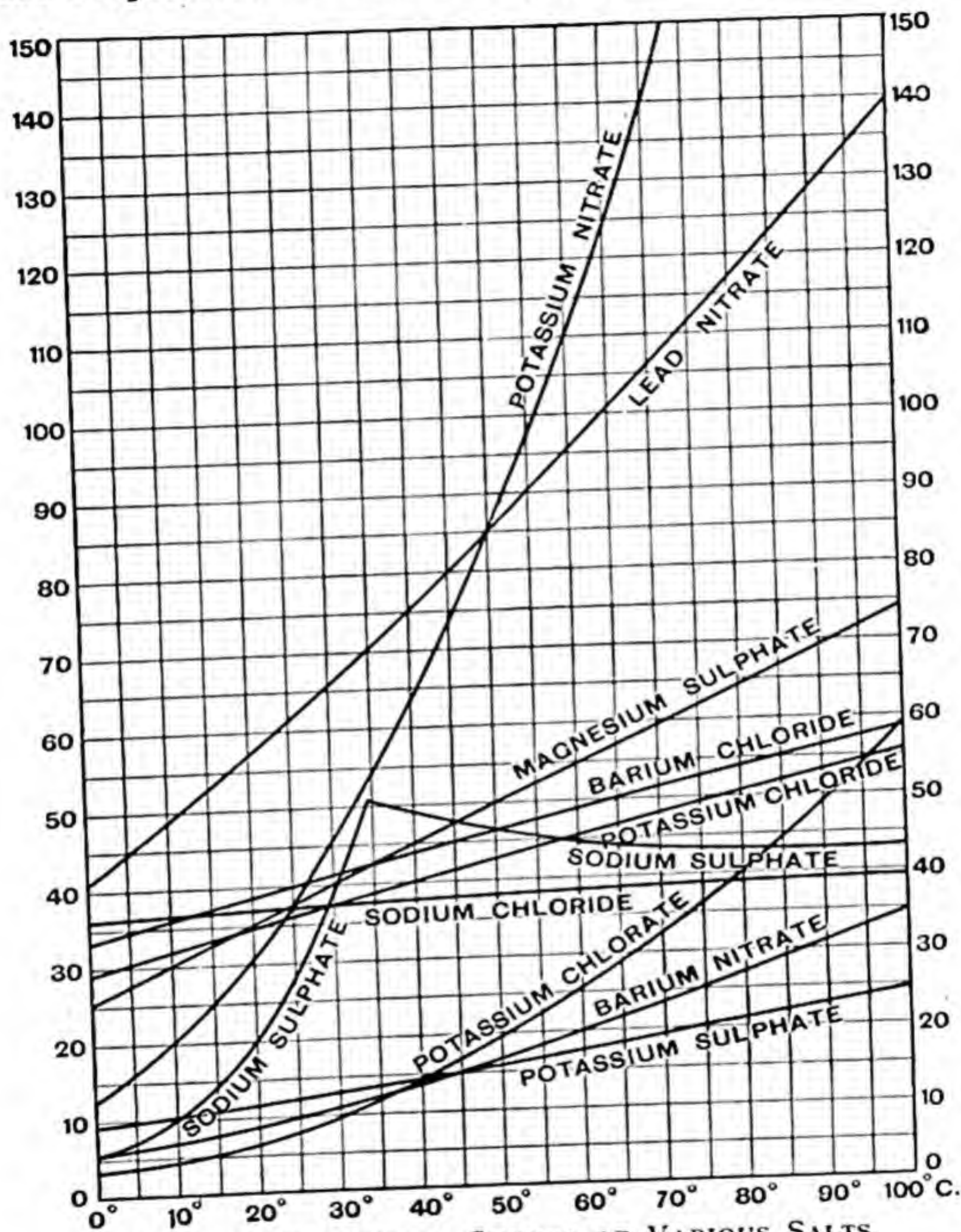


FIG. 41.—SOLUBILITY CURVES OF VARIOUS SALTS, SHOWING THE EFFECT OF TEMPERATURE ON SOLUBILITY.

Solubility depends (1) on the chemical characters of the solute and solvent, *e.g.* common salt is less soluble than 'hypo' in water and both salts are nearly insoluble in alcohol; and (2) on the temperature, generally but not always increasing with

rise of temperature. The rather uncommon case of diminution of solubility with rise of temperature may be shown by placing a tube containing calcium butyrate solution, saturated at the ordinary temperature, in a beaker of boiling water. In a short time crystals of the salt separate. These redissolve on cooling.

The dependence of solubility on temperature is most conveniently represented graphically by means of solubility curves, in which the abscissae (horizontal distances) represent temperatures, and the ordinates (vertical distances) the solubilities. In Fig. 41 the solubility curves of some salts in water are exhibited. It will be seen that these vary very considerably. The solubility of some salts (*e.g.* potassium nitrate) increases rapidly as the temperature rises. Others, such as sodium chloride, are not much more soluble at higher temperatures than at room temperature, and some salts, such as sodium sulphate, become less soluble at higher temperatures. These curves have been constructed by the method described in the next paragraph.

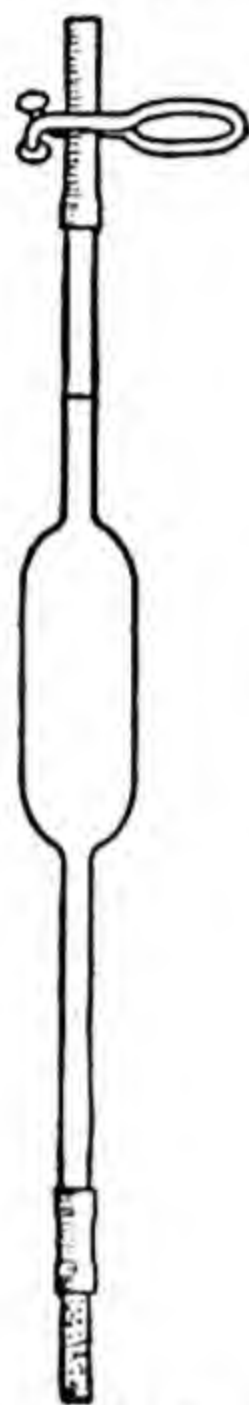


FIG. 42.—PIPETTE FOR DETERMINATION OF SOLUBILITY.

**Determination of solubility.**—The solubility of a salt at various temperatures is best determined by stirring the powdered solid salt with water at the given temperature, so that excess of solid is present, withdrawing a portion of the clear solution, weighing it, and then evaporating the solution in a weighed dish to find the weight of solid salt contained in it.

A pipette is fitted with pieces of rubber tubing at each end. The upper piece of rubber is closed by a clip, whilst the lower piece is connected with a short piece of tubing, packed with glass wool, to serve as a filter (Fig. 42). The pipette is cleaned and dried. A quantity of powdered potassium nitrate is now stirred with water in a 250 c.c. beaker, set in a water-bath, and the temperature kept at  $20^{\circ}$ , as shown by a thermometer in the beaker. When the mixture has been stirred for some minutes, the filter is attached to the pipette, and solution drawn into the latter. The filter is detached, and the solution run from the pipette



into a weighed dish; this is allowed to cool and weighed again to find the weight of solution. The liquid is then evaporated and the dry residue weighed. The experiment is repeated at  $30^{\circ}$ ,  $40^{\circ}$ , and  $50^{\circ}$ , and the solubilities, in grams per 100 gm. of water, plotted against the temperatures (Fig. 41).

The following results were obtained with two salts: the corresponding curves are plotted in Fig. 41.

		$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$40^{\circ}$	$60^{\circ}$	$80^{\circ}$	$100^{\circ}$
Potassium nitrate -	-	13.3	20.9	32	64	110	169	246
Sodium sulphate { (Glauber's salt) }	-	5.0	9.0	19.4	49	45	44	42

The curve for Glauber's salt really consists of two curves meeting at a sharp angle at  $33^{\circ}$ .

**Hydrates and anhydrous substances.**—Large clear crystals of washing-soda, when exposed to the air, become white and opaque and fall to powder. There is also loss in weight. The change is due to loss of water from the crystals, and is called **efflorescence** (p. 45).

Many salts form crystals of definite composition, called **hydrates**,\* containing water. The water of hydration is usually known as **water of crystallisation**. It is found that large crystals are deposited when the crystallisation takes place slowly. Very large crystals of alum, for example, may be obtained by allowing a solution, saturated at the ordinary temperature, to evaporate slowly in the air, and suspending a small perfect crystal in the solution by a thread. If a solution is cooled rapidly, and stirred, small crystals are deposited. These are usually purer than the large crystals, since they are less likely to include liquid.

A salt which crystallises without water is said to be **anhydrous**. Common salt, sal ammoniac, potassium nitrate, sodium nitrate, potassium chlorate and potassium dichromate are all anhydrous, and this should be remembered. A salt which usually crystallises with water may often be rendered anhydrous by heating, when the water of crystallisation is driven off. For example, blue crystals of hydrated copper sulphate (*blue vitriol*) when heated fall to a white powder of anhydrous copper sulphate (Fig. 43).

\* Notice carefully the difference between a *hydrate* (a compound of a substance with *water*) and a *hydroxide* (a compound of an element or radical with the *hydroxide* radical, OH; see p. 146). Some *hydroxides* readily lose water on heating, forming oxides (*e.g.* calcium hydroxide, or slaked lime). In older books, hydroxides are sometimes called **hydrates**.

This powder at once takes up water again when moistened, and becomes blue. This fact is made use of in testing for the presence of water in anhydrous (or 'absolute') alcohol. The white powder also slowly turns blue on exposure to air, by absorbing moisture from the latter.

Solutions, or hydrated crystals, of cobalt chloride are pink, but on heating the crystals lose water and become blue. They also become blue when exposed to *dry* air, and a device for indicating the dryness of the atmosphere has been based on this

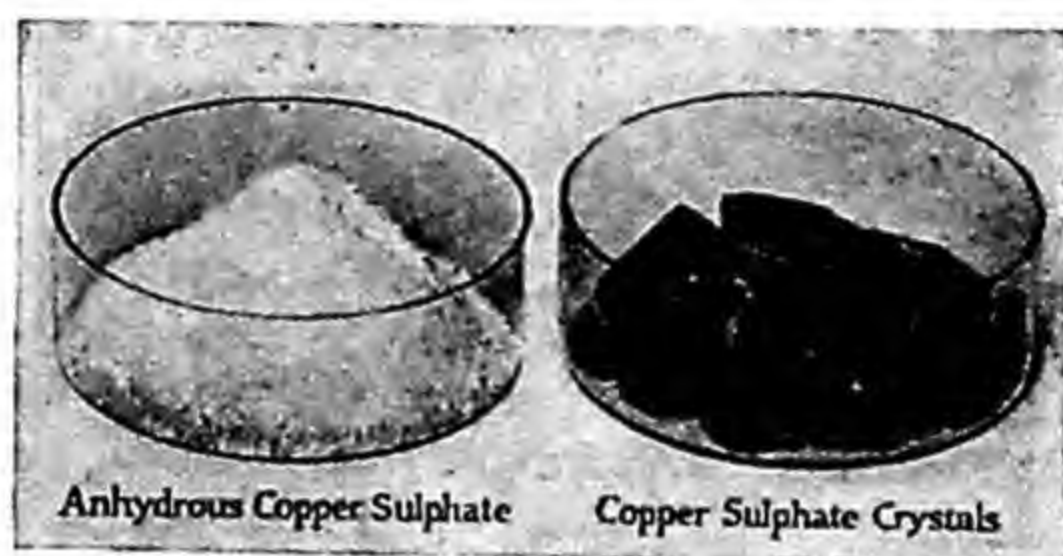


FIG. 43.—CRYSTALS OF COPPER SULPHATE HYDRATE AND THE AMORPHOUS ANHYDROUS SOLID FROM AN EQUAL WEIGHT OF CRYSTALS.

fact. Since the blue colour is more intense than the pink, writing on paper done with weak cobalt chloride solution is invisible when dry, but on holding the paper before the fire the water of crystallisation is driven off from the cobalt chloride and the letters appear, in green or blue. They fade again when exposed to air by taking up moisture. Cobalt chloride solution can therefore be used as an 'invisible,' or 'sympathetic,' ink.

**The freezing of solutions.**—The ice formed when sea water freezes yields fresh water on melting.

The solid separating when solutions freeze is usually pure ice: all the solute remains in the still liquid portion. Thus, freezing, as well as distillation, will enable us to separate the constituents of a solution. The solution remaining will become increasingly richer in salt as more and more ice separates.

The freezing point of a solution is lower than that of the pure solvent (Fig. 44). It is found by experiment that the freezing point is lowered *proportionally* to the concentration of dissolved substance. A limit is reached when so much solvent has separated in the solid state by freezing that the amount remaining in the liquid is only just sufficient to keep the salt in solution.



On further cooling, both ice and salt will then separate together in the solid state in the proportions in which they exist in the solution, and the temperature remains constant. This minimum temperature ( $-22^{\circ}\text{C}$ . in the case of common salt), which is the same as that of a mixture of ice and solid salt, is called the *cryohydric*, or *eutectic temperature*. *Dissolved substances lower the freezing point of a solvent.*

The lowering of freezing point of water caused by adding alcohol or glycerine is utilised in countries which have very severe winters to prevent the freezing of water in motor car radiators and cooling systems.

The melting of snow in streets by strewing it with salt is another application of the same effect. A mixture of ice and salt is used in freezing ice-cream. A different kind of freezing mixture makes use of the considerable absorption of heat which results when many salts, such as ammonium nitrate, dissolve in water. A mixture of salts (e.g., ammonium chloride, potassium nitrate and sodium sulphate) may also be used.

It should also be remembered that *dissolved substances raise the boiling point of a solvent.*

In the laboratory a bath of a boiling solution of calcium chloride (easily soluble) is used to obtain a higher temperature than a water bath.

**Fractional crystallisation.**—Just as fractional distillation is employed in the purification of liquids by making use of the fact that different liquids have different boiling points, so **fractional crystallisation** may be used in the purification of solids by making use of their different solubilities, and particularly the fact that the solubilities of some salts increase more rapidly with rise of temperature than those of other salts. The theory of the process is most clearly seen from the solubility curves (Fig. 41).

Consider a mixture of *potassium nitrate* and *sodium chloride*. It is seen that 100 gm. of water at  $65^{\circ}$  dissolve 120 gm. of potassium nitrate but only 37 gm. of sodium chloride. If a mixture of equal parts of the two salts is heated with an amount of water

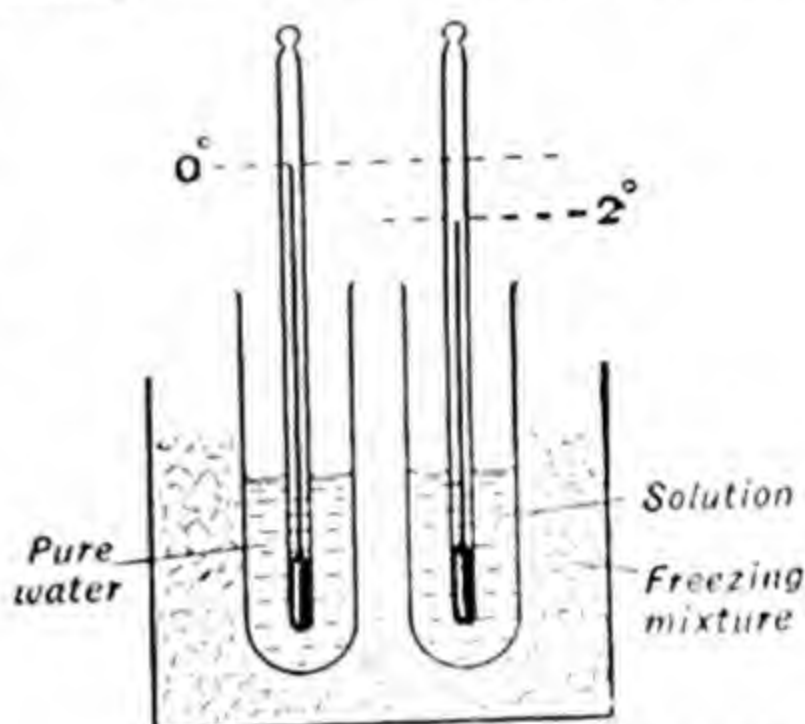


FIG. 44.—DEPRESSION OF FREEZING POINT OF WATER CAUSED BY A DISSOLVED SUBSTANCE.

PURE WATER FREEZES AT  $0^{\circ}\text{C}$ .; SEA WATER, CONTAINING DISSOLVED SALT, FREEZES AT  $-2^{\circ}\text{C}$ .

insufficient to dissolve all the sodium chloride, the whole of the potassium nitrate will go into solution, together with some sodium chloride.

Now let the solution be poured off from the undissolved sodium chloride, and allowed to cool to room temperature, say  $15^{\circ}$ . At this temperature 100 gm. of *pure water* is saturated by 25 gm. of potassium nitrate, so that a considerable amount of this salt will separate from the solution. A small amount of sodium chloride will also separate, since its solubility at  $15^{\circ}$  is about 36. This small amount of sodium chloride may be removed from the potassium nitrate either by repeating the process of crystallisation, when all the sodium chloride will remain in solution, or by washing the crystals with ice-cold water, in which potassium nitrate, as is seen from the curves, is much less soluble than sodium chloride, so that the latter is removed.

A variation of the process is used in making potassium nitrate for the manufacture of gunpowder. Sodium nitrate is much cheaper but is unsuitable for gunpowder because it becomes damp on exposure to moist air. A mixture of sodium nitrate and potassium chloride is dissolved in hot water, when a solution is obtained from which potassium nitrate and sodium chloride are separated as explained above.

It is not possible to make calculations as to the amounts of the two salts dissolved at different temperatures from the mixture, since the solubility of one salt is not the same in presence of another salt as in pure water. Usually one salt lowers the solubility of another, but not always.

It is clear that a greater number of crystallisations will be required to separate salts which are nearly equal in solubility, such as barium chloride and potassium chloride. Isomorphous salts (*see p. 187*), *i.e.* salts crystallising in the same form, cannot be separated by crystallisation, since the crystals deposited from the solution contain both salts.

Fractional crystallisation is frequently used on the technical scale for the separation and purification of materials. It may be that only a small amount of the desired material is present with a large quantity of other materials, and then a rather laborious process is necessary. In the separation of the element radium in laboratory experiments its discoverer, Madame Curie, obtained only a fraction of a gram of radium salt after a very long and tedious process of fractional crystallisation from some tons of natural material, the uranium ore called pitchblende.

The mantles used in incandescent gas burners contain a metallic



oxide called **thoria**, together with a small amount of another called **ceria**, both obtained from a mineral called **monazite**. Thoria and ceria are members of a group of substances called

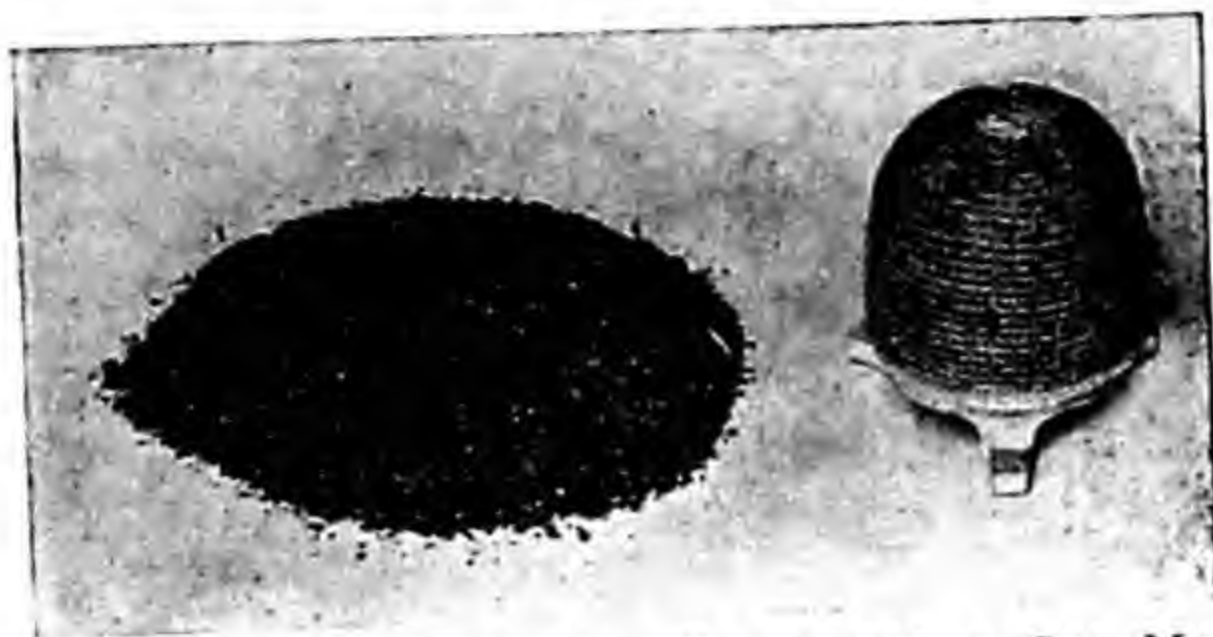


FIG. 45.—HEAP OF MONAZITE SAND AND A GAS MANTLE.  
THE THORIA AND CERIA USED IN THE GAS MANTLE ARE EXTRACTED  
BY CRYSTALLISATION OF THEIR SALTS.

**rare earths**, because some of them occur only in small quantities in a few localities. The rare earth minerals often contain several earths and the separation may involve hundreds of crystallisations.

**Vapour pressure.**—A little petrol spilled on the floor of a garage rapidly evaporates, or dries up, whilst lubricating oil remains without evaporation for an indefinite period. Petrol is called a **volatile liquid** and oil a **non-volatile liquid**. Liquids differ in volatility: petrol is more volatile than water. Why are some liquids more easily evaporated than others? This is made clear by an experiment.

A few drops of water are introduced into the vacuous space of a barometer tube; it will be seen that the mercury level at once falls (Fig. 46). At a fixed temperature the mercury level assumes another constant position, provided that excess of liquid is present in the space above. The fall in level represents the **vapour pressure** exerted by the liquid in equilibrium with its **saturated vapour** (see Hadley's *Everyday Physics*, p. 244).

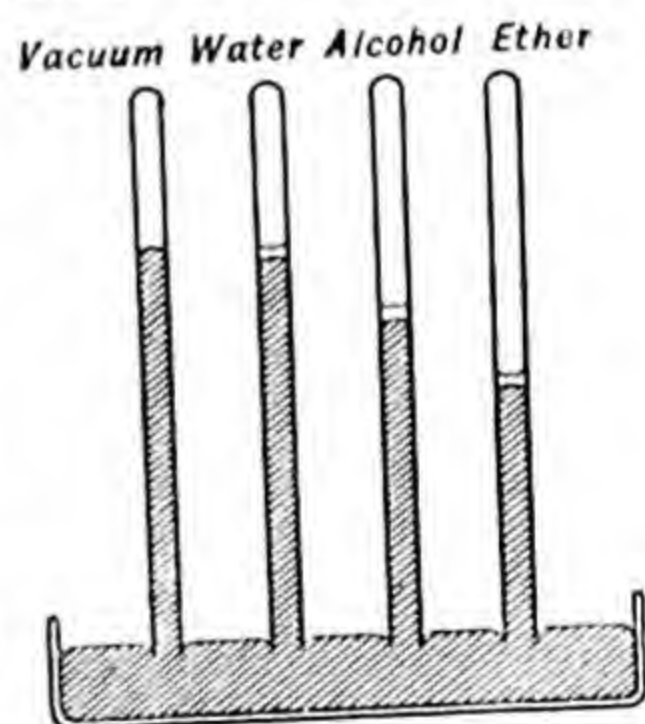


FIG. 46.—LIQUIDS INTRODUCED INTO BAROMETER TUBES AND EXERTING DIFFERENT VAPOUR PRESSURES.

If the experiment is repeated with alcohol and with ether, it will be found that these liquids have vapour pressures greater than that of water, and the vapour pressure of ether is greater than that of alcohol. The higher the vapour pressure of a liquid the more easily the liquid evaporates. Volatile liquids have lower boiling points than less volatile liquids.

Just as there are unsaturated and supersaturated solutions, so there are **unsaturated vapours** and **supersaturated vapours**, which take up more liquid, or deposit liquid, respectively, when brought in contact with liquid.

The atmosphere always contains a certain amount of water vapour, but it is rarely saturated, so that water usually evaporates when exposed to the air.

**Vapour pressures of solutions : deliquescence.**—The vapour pressure of a solution may be determined in the same way as

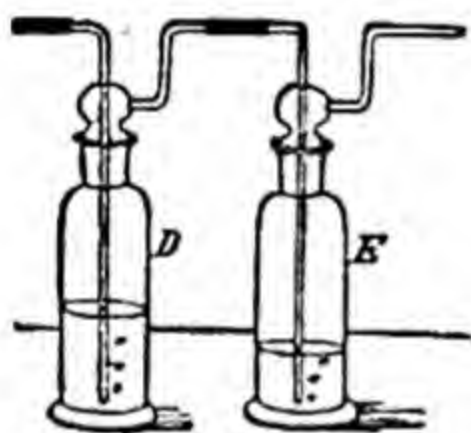


FIG. 47.—WASH BOTTLES FOR PURIFYING AND DRYING GASES.

that of water: it is usually smaller than the vapour pressure of water, and more concentrated solutions are found to have smaller vapour pressures than dilute ones. Very soluble substances can thus form saturated solutions which have vapour pressures smaller even than the pressure of water vapour existing in the atmosphere. They can attract moisture from, and they gradually become liquid, or deliquesce, on exposure to, the

air. Calcium chloride, caustic soda, magnesium chloride and potassium carbonate are deliquescent substances and must be kept in tightly closed bottles. Impure table salt (sodium chloride) usually contains small amounts of calcium and magnesium chlorides and deliquesces, or becomes damp, on exposure to air. If the common salt is mixed with sodium carbonate and phosphate, which convert the deliquescent salts into the insoluble non-deliquescent magnesium and calcium carbonates and phosphates, the table salt ceases to be deliquescent and can be poured out from the containers. *Cereba* salt is of this type. Even this salt becomes damp on exposure to very moist air, since then the vapour pressure of the saturated sodium chloride solution is less than the pressure of the water vapour in the air.

Some substances, such as quicklime, dry wool and anhydrous copper sulphate, absorb water vapour from the air but do not become liquid. They are called **hygroscopic**. Woollen garments



which have been 'aired' and feel quite dry usually steam when held before a fire.

Deliquescent substances absorb moisture and may be used to remove it from gases. Calcium chloride, caustic potash or soda, and phosphorus pentoxide are commonly employed. Quicklime and concentrated sulphuric acid, which are hygroscopic materials, are also used. The liquid acid may be used in wash-bottles (Fig. 47) and a stream of gas bubbled through it, or it may be absorbed in pumice, the pieces of pumice soaked in acid being put into a drying tower (Fig. 48) and a stream of gas passed through the tower. Solid drying agents, such as calcium chloride, are usually contained in U-tubes or drying towers.

Solids are dried by keeping them in air over one of the above substances in a closed glass vessel called a desiccator (so called from the Latin *siccus*, dry). A common form of desiccator is shown in Fig. 49. The drying agent is in the lower half and the lid is an accurate fit on a ground flange, which is greased.

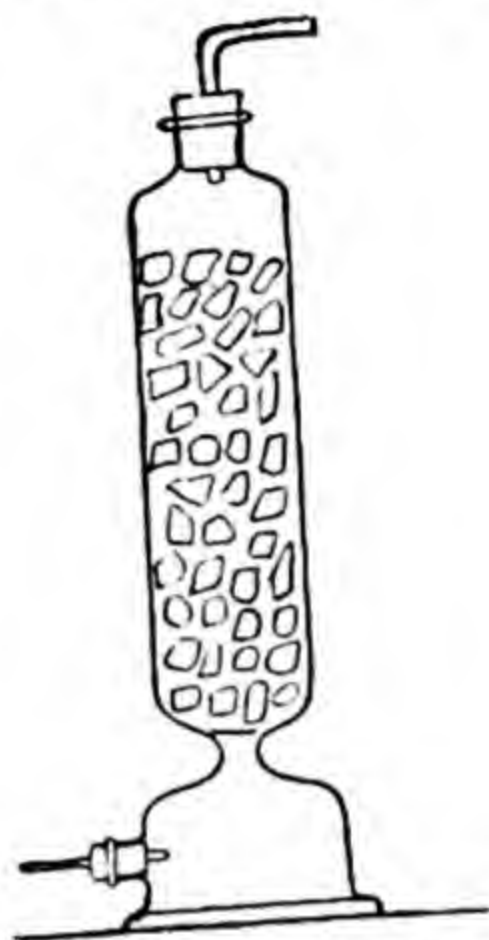


FIG. 48.—DRYING TOWER FOR DRYING GASES.



FIG. 49.—DESICCATOR.

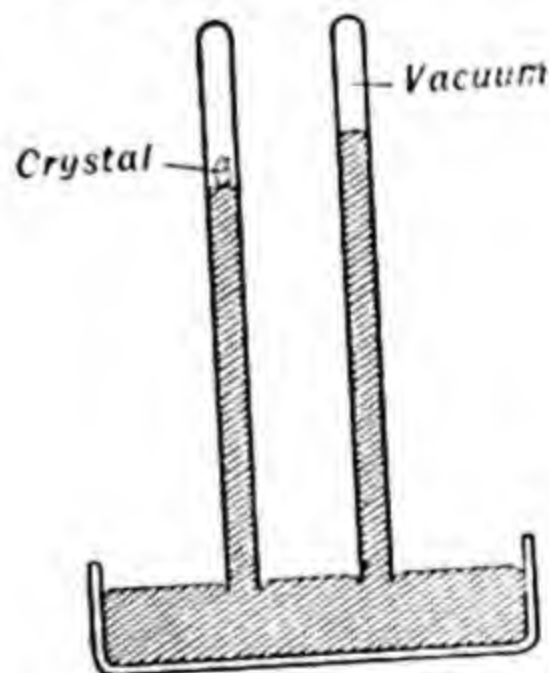


FIG. 50.—VAPOUR PRESSURE OF A CRYSTAL HYDRATE.

**Vapour pressures of hydrates : efflorescence.**—If a crystal of a hydrated salt, such as washing soda or hydrated copper sulphate, is passed into a barometer tube, it exhibits a definite vapour pressure (Fig. 50). If this is greater than the pressure

of the water vapour in the atmosphere, the crystal will lose water on exposure, and effloresce (p. 46). The rapidity of efflorescence is increased by suspending the crystal in a desiccator, whilst if the crystal is suspended in a test-tube containing a little water, so as to saturate the air with water vapour, it does not effloresce. Efflorescence is more rapid when the crystal is heated, since the vapour pressure is then increased.



## CHAPTER III

### ELEMENTS AND COMPOUNDS

**Chemical changes.**—It is a matter of common observation that bodies often undergo radical changes under certain conditions. Thus, milk may become sour ; bright copper becomes dull, and ultimately covered with a green crust, when exposed to moist air, and under the same conditions iron rusts away completely to a brown powder. A candle burns away, and apparently disappears.

In other cases the changes appear to be much less deep-seated, and the properties of the materials are only slightly, and temporarily, modified. Thus, water on cooling freezes to ice, but the ice melts, and is reconverted into water, on warming. A bar of iron which has been heated to redness is only slightly altered and, apart from a little scale on the surface, is recovered without change on cooling. A piece of platinum wire when heated in a Bunsen flame becomes red hot, but is unchanged on cooling. A piece of copper wire becomes covered with black scales when heated, whilst a piece of magnesium wire on heating takes fire and burns brilliantly, leaving a white ash.

Material changes either affect only a few properties of the material, and are temporary, when they are called **physical changes** ; or they are much more drastic, resulting in the disappearance of the original material as such, and the formation of a different material, when they are called **chemical changes**. The following experiments illustrate some striking chemical changes.

A small piece of yellow phosphorus placed on a sand-tray is sprinkled with a few crystals of iodine. The phosphorus takes fire.

Dilute solutions of potassium ferrocyanide, tannin and potassium thiocyanate, which are all practically colourless, are poured into three glasses, and to them a dilute solution of ferric chloride acidified with a little hydrochloric acid, also practically colourless, is added. Blue, black and red solutions are formed.

A small pill of mercuric thiocyanate heated by the flame of a taper swells up into a worm-like mass of a friable yellow substance ('Pharaoh's Serpent').

A mixture of 5 parts of fine iron filings and 3 parts by weight of flowers of sulphur is heated in a test-tube (Fig. 51). The sulphur boils, and then the iron begins to glow, and continues to do so when the tube is removed from the flame. When the glowing ceases, the tube is heated for a short time, then allowed to cool by placing it on a tray of sand. When cold, the tube is broken in a mortar. A greyish mass is obtained, which is easily powdered in the mortar. The powder is black, and

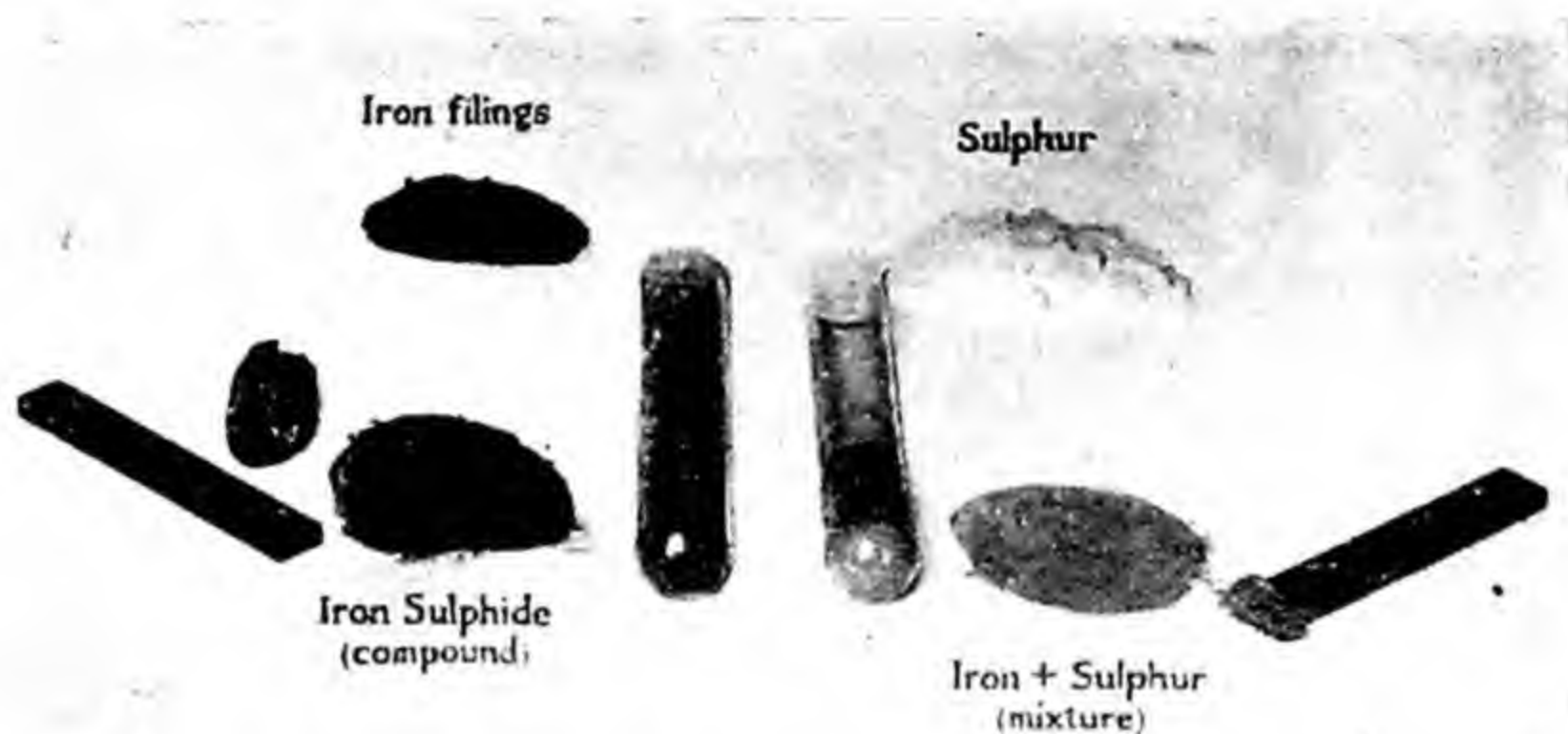


FIG. 51.—EXPERIMENT ILLUSTRATING THE FORMATION OF A COMPOUND, IRON SULPHIDE, ON HEATING A MECHANICAL MIXTURE OF IRON AND SULPHUR.

under a lens no iron or sulphur particles can be distinguished in it, although these can be seen in the mixture. It yields no sulphur when treated with carbon disulphide, which dissolves sulphur from the mixture, and if a magnet is brought over it iron is not attracted, as it is from the mixture. The iron and sulphur have formed a new substance, called **iron sulphide**.

From these experiments it is seen that chemical changes are often accompanied by an evolution of heat. This, however, is by no means always the case. At times sometimes heat is absorbed.

When concentrated hydrochloric acid is poured over crystals of Glauber's salt in a beaker, the crystals fall to a granular white powder of common salt. A considerable absorption of heat occurs, and water in a small test-tube placed in the beaker is



frozen. This is an example of a chemical change accompanied by absorption of heat.

**Characteristics of physical and chemical changes.**—Some of the main characteristics of chemical and physical changes may now be summarised :

**I. Physical changes :** no new substance is produced : if anything more than mere heating or cooling is involved, it is usually merely a change of state (melting, evaporation) : apart from latent heat absorbed or evolved in changes of state, and heat supplied to or removed from a body, there is no marked evolution or absorption of heat : the change is easily reversed by appropriate alteration in the external conditions : the weight of the material remains unchanged.

**II. Chemical changes :** new substances with different properties are produced : the change is generally attended by evolution of heat (sometimes by absorption of heat), and sometimes (as in combustion) of light : the change is not easily reversed by mere change of external conditions unless the system is in a state of equilibrium : the weight of the material usually changes when it is converted into the new substance.

Chemical changes occur very easily between *dissolved* substances, on account of the extremely fine state of subdivision of such substances (p. 32).

**The law of indestructibility of matter.**—Although the weight of a material usually alters when the substance undergoes chemical change, *e.g.* the white powder formed by burning magnesium in air is heavier than the magnesium, this may always be traced to the addition or removal of some other substance. In some cases the weight seems to diminish, as in the burning away of a wax candle. The following very instructive experiment shows that in such cases there is really no destruction of matter.

A small candle is fitted through a cork, with holes bored to

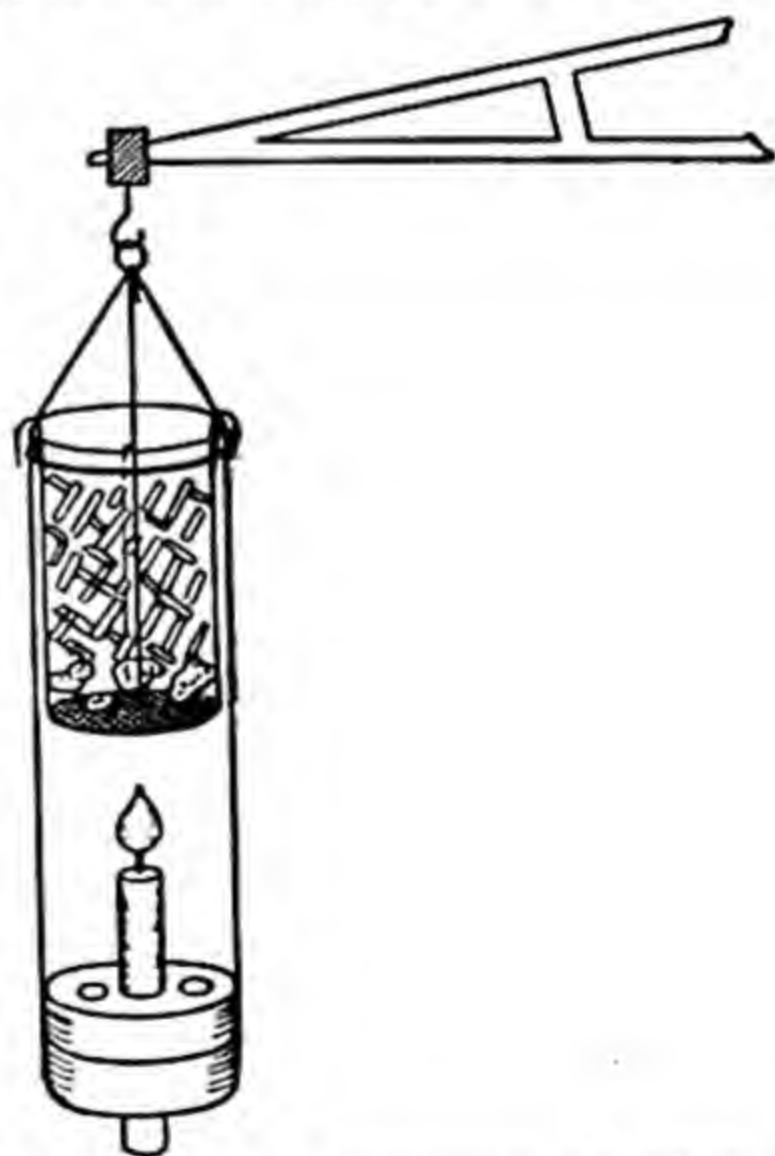


FIG. 52.—BURNING A CANDLE SO AS TO RETAIN THE PRODUCTS OF COMBUSTION.



FIG. 53.

OTTO VON GUERICKE'S AIR PUMP, SHOWN ON THE LEFT BELOW. ON THE RIGHT BELOW IS THE GLOBE FOR WEIGHING AIR. ON THE RIGHT AT THE TOP ARE THE FAMOUS 'MAGDEBURG HEMISPHERES.'



admit air, into a glass tube in which a piece of wire-gauze is supported. Sticks of caustic soda, on a few pieces of quicklime, are placed on the top of the gauze, and the whole apparatus is counterpoised on a balance (Fig. 52). The candle is lit, and allowed to burn. In a few minutes the arm of the balance carrying the apparatus is depressed, showing that, so far from a loss of weight occurring when a candle burns, there is an increase of weight *if the products of combustion are prevented from escaping* by absorption in quicklime and caustic soda. The nature of these products may be found by the following experiments.

A cold glass jar is held over a candle flame: the inside immediately becomes bedewed with moisture, showing that water is formed in the combustion. A little lime water is poured into the jar and shaken round: it becomes turbid. This is a test for carbon dioxide, showing that this gas is also produced. The water and carbon dioxide are both held back by the quicklime and caustic soda, and the experiment makes it probable that something is taken from the air during the combustion of the candle, which forms water and carbon dioxide with the materials of the wax. If this is the case, *air must possess weight*. Although the ancients believed that air was without weight, the opposite was proved in 1654 by the following experiment of Otto von Guericke, the inventor of the air-pump (Fig. 53).

A glass globe fitted with a stopcock (Fig. 54) is exhausted by an air-pump, and counterpoised on the balance. Upon opening the stopcock a hissing noise is heard, due to the air rushing into the globe. When the globe is replaced on the balance, it will be noticed that the side of the beam on which it hangs is depressed owing to the increase in weight of the globe when filled with air. This increase is determined by adding weights to the opposite side, and it will be found that a litre of air weighs a little more than one gram, so that water is about a thousand times as dense as air. The original apparatus used by Guericke is shown in Fig. 53.

In order to put to the test the question of the constancy of total weight in chemical change, it is obvious that the chemical change, or **chemical reaction** as it is usually called, must be instituted in a closed space, so that none of the materials can escape. The experiment with the candle is not decisive in this respect, since it does not enable us to find the weight of the air, or part of the air, concerned in the combustion. Since a candle is not easily kindled in a closed space, it is more convenient to

use a small piece of phosphorus, which readily ignites on warming.

A *small* piece of white phosphorus is quickly dried between filter papers and placed in a strong 250 c.c. round-bottom flask, tightly closed by a good rubber stopper. The flask is weighed. The phosphorus is warmed till it ignites. When the combustion has ceased the flask is allowed to cool, and is re-weighed. The weight is unchanged, although an evident chemical change has occurred.



FIG. 54—GLOBE FOR WEIGHING AIR.

Another kind of chemical reaction occurs in solutions. A little ferric chloride solution in a test-tube is placed inside a flask containing potassium ferrocyanide solution, and the flask corked and weighed (Fig. 55). On tilting the flask, the liquids mix and a deep blue precipitate forms. The flask is reweighed. There is no change in weight, although a chemical change has occurred.

These experiments show that, in the cases investigated, *there is no change in total weight when a chemical reaction occurs*, or that the total weight of the products of the reaction is equal to the total weight of the substances which entered into reaction. Numerous experiments have proved that this result is quite general: it constitutes a law of Nature, called the **Law of Indestructibility of Matter**, or the **Law of Conservation of Mass**. This name is used because the weight or mass of a body is considered to be a measure of the quantity of matter in it.

Some important applications of the law of conservation of mass are considered in the next paragraph.

**Elements and compounds.**—Substances may undergo chemical changes in one of two ways, according to their composition. Either the substance increases in weight in all the changes which it undergoes; or it gives other substances, each of less weight than the original substance, or, as is said, it **decomposes**.

This result has been found by appropriate experiments, of which the following are typical.



FIG. 55.—CHEMICAL REACTION IN A CLOSED SPACE WITHOUT CHANGE IN WEIGHT.



Let 0.5 gm. of **magnesium** ribbon be heated in a weighed, loosely covered, porcelain crucible (Fig. 56) over a small flame till combustion ceases. Then let it be heated strongly for ten minutes with the lid off, cooled and weighed. There will be an *increase in weight*, which, if the experiment is performed carefully, will amount to 0.333 gm. The magnesium has combined with oxygen from the air.



FIG. 56.—HEATING MAGNESIUM WITH ACCESS OF AIR; A COMPOUND, MAGNESIUM OXIDE, IS FORMED.

Next suppose that a weight of 2.16 gm. of red oxide of mercury (**mercuric oxide**) is placed in a weighed, hard glass tube, connected by a rubber stopper with a glass delivery tube leading to a pneumatic trough in which is inverted a measuring cylinder full of water, the mouth of which is over the delivery tube (Fig. 57). On heating, the red substance blackens, and bubbles of gas collect in the cylinder. At the same time, a shining metallic sublimate of mercury collects on the cooler part of the glass tube. When the evolution of gas ceases and the oxide has disappeared, the delivery tube is removed from

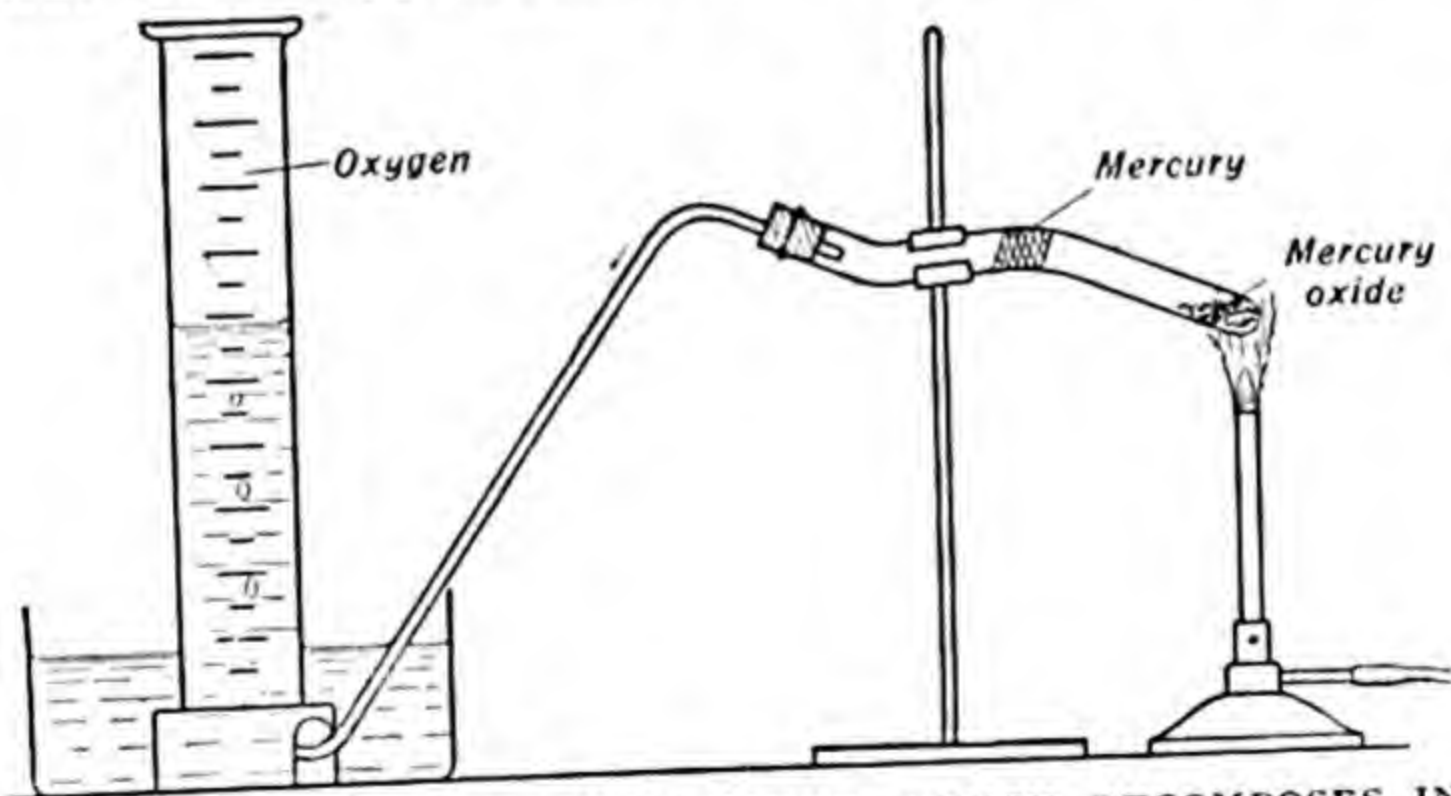


FIG. 57.—HEATING MERCURIC OXIDE, WHICH DECOMPOSES INTO METALLIC MERCURY AND OXYGEN GAS.

the trough and the apparatus is allowed to cool. The tube is again weighed, and will be found to have lost in weight. If the experiment has been carefully performed, the *loss in weight* should amount to 0.16 gm. The volume of gas collected will

be about 118 c.c. If a glowing chip of wood is placed in the gas, it is rekindled, and burns with a brilliant flame, indicating that the gas is **oxygen**.

If a pure substance can be decomposed into two or more substances of smaller weight, as the red oxide of mercury into mercury and oxygen gas, we say that it is a **compound**. If it always yields substances of greater weight, indicating that, in all reactions in which it takes part, combination occurs with other substances, and never decomposition, the substance is called an **element**. Magnesium is an element.

It is clear that the experimental distinction between elements and compounds depends on the law of indestructibility of matter, since the *total* weight must remain unchanged.

**Analysis and synthesis.**—The process by which a compound is separated into its constituent elements, *e.g.*, the decomposition of red oxide of mercury by heat, is called **analysis**, from the Greek *analuo*, I unloose. The building up of a compound from its elements, as in the production of magnesium oxide by heating magnesium in air, is called **synthesis**, the Greek word *synthesis* meaning a putting together. The process of ascertaining the composition of substances is also called analysis; **qualitative analysis** leads to a knowledge of the constituents only, without finding the proportions in which they are combined, whilst **quantitative analysis** determines these proportions in addition.

**Compounds are constant in composition.**—The composition of a compound is independent of the method of preparation.

The same compound, also, gives the same elements in the same proportions, no matter what means are used for its decomposition. This may be illustrated by the following experiments.

Metallic tin may be converted into oxide of tin in two different ways :

(a) One gm. of tinfoil may be weighed into a counterpoised Rose's crucible (Fig. 58), and heated in a stream of oxygen passed through the porcelain tube through a small hole in the lid of the crucible. The crucible is cooled and weighed from time to time until its weight becomes constant. The residue is oxide of tin.

(b) One gm. of tinfoil may be weighed into a counterpoised porcelain basin, covered with a large watch-glass. It is treated carefully with successive small amounts of strong nitric acid



FIG. 58.—ROSE'S CRUCIBLE.



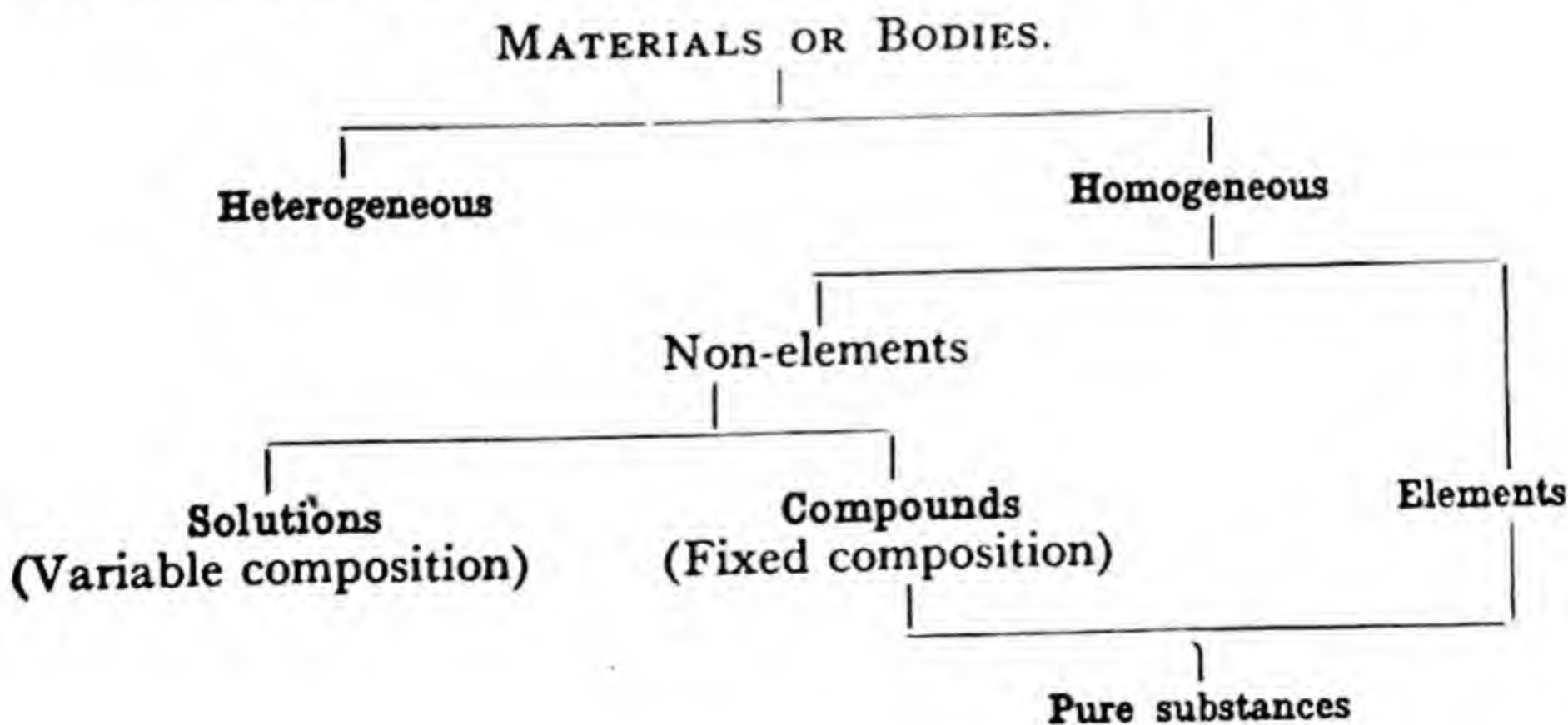
until the violent action ceases, the watch-glass being placed over the basin after each addition to prevent loss by spiriting. The solid on the glass is washed into the dish, the excess of acid is then evaporated off on a sand-bath, and the material is heated for ten minutes over a Bunsen flame. The dish is cooled and weighed. The residue is oxide of tin.

It will be found that, within the limits of experimental error, the weight of oxide of tin obtained from 1 gm. of tin in the two different methods is the same. Hence the composition of oxide of tin is constant, and independent of the method of preparation. Oxide of tin is, therefore, a compound, not a mixture or a solution.

The distinction between **chemical compounds** and **mechanical mixtures** is simple, but that between **compounds** and **solutions**, both of which are homogeneous, requires further consideration. Solutions of common salt in water may vary in composition from pure water to a saturated solution of salt, and between these limits an indefinite number of compositions is possible. Oxide of mercury, on the other hand, always has the same composition, 100 parts of mercury and 8 parts of oxygen. Substances such as oxide of mercury, *of constant composition*, are called **compounds**; homogeneous materials such as salt water, *of variable composition*, are called **solutions**.

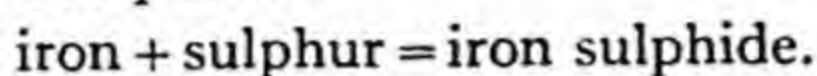
Solutions are always separable, by suitable means, into two or more **pure substances**, either elements or compounds. Thus, solutions of salt in water are separated into these two constituents by simple evaporation.

The arrangement in the following table, which summarises the contents of the preceding paragraphs, should be carefully noted.

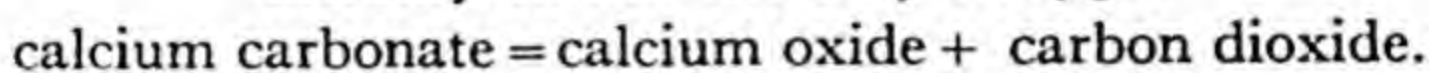
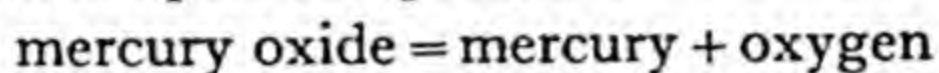


**Types of chemical change.**—Although practically all chemical changes may be regarded as made up of combinations and decompositions, it is usual to recognise in all five types of chemical change :

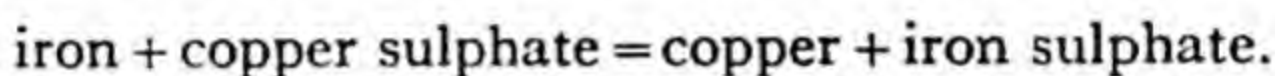
(1) **Combination** : two or more elements combine to form a definite chemical compound :



(2) **Decomposition** : a compound decomposes into two or more elements, or into simpler compounds :

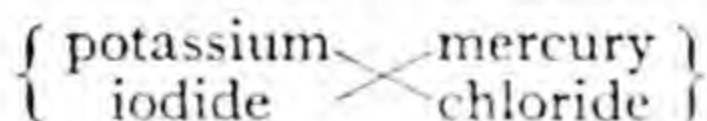
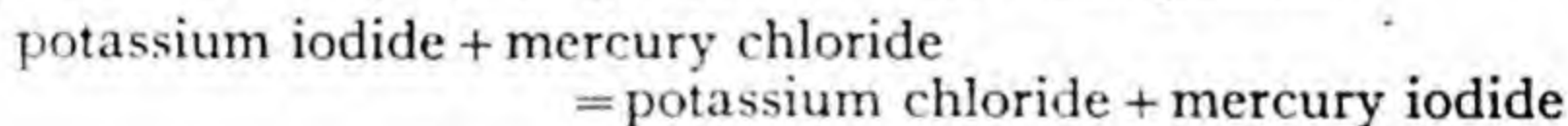


(3) **Replacement** : one element replaces another in a compound :



A clean piece of iron dipped into copper sulphate solution becomes coated with a red deposit of copper, whilst iron goes into solution.

(4) **Double decomposition** : two compounds interact chemically by exchange of parts to produce two new compounds :



Clear colourless solutions of these two salts when mixed at once throw down a precipitate of solid insoluble mercury iodide. This is at first yellow, but quickly becomes red. Potassium chloride remains in solution, as may be found by filtration and evaporation.

(5) **Isomeric change** : when red mercury iodide is heated it becomes yellow, and *remains* yellow on cooling. (Many substances change colour on heating but recover the original colour on cooling : e.g., zinc oxide is yellow when hot but becomes white again on cooling.) The yellow form, which is a second variety of mercury iodide, becomes red again when rubbed with a glass rod. This is an example of a *substance changing into another form with different properties but the same composition*, and is called an isomeric change.

Even elements can exist in different forms. The diamond, graphite or black lead, and charcoal are merely different forms



(allotropic forms) of the same element, carbon (Fig. 59). Black lead and diamonds can both be obtained from charcoal. The

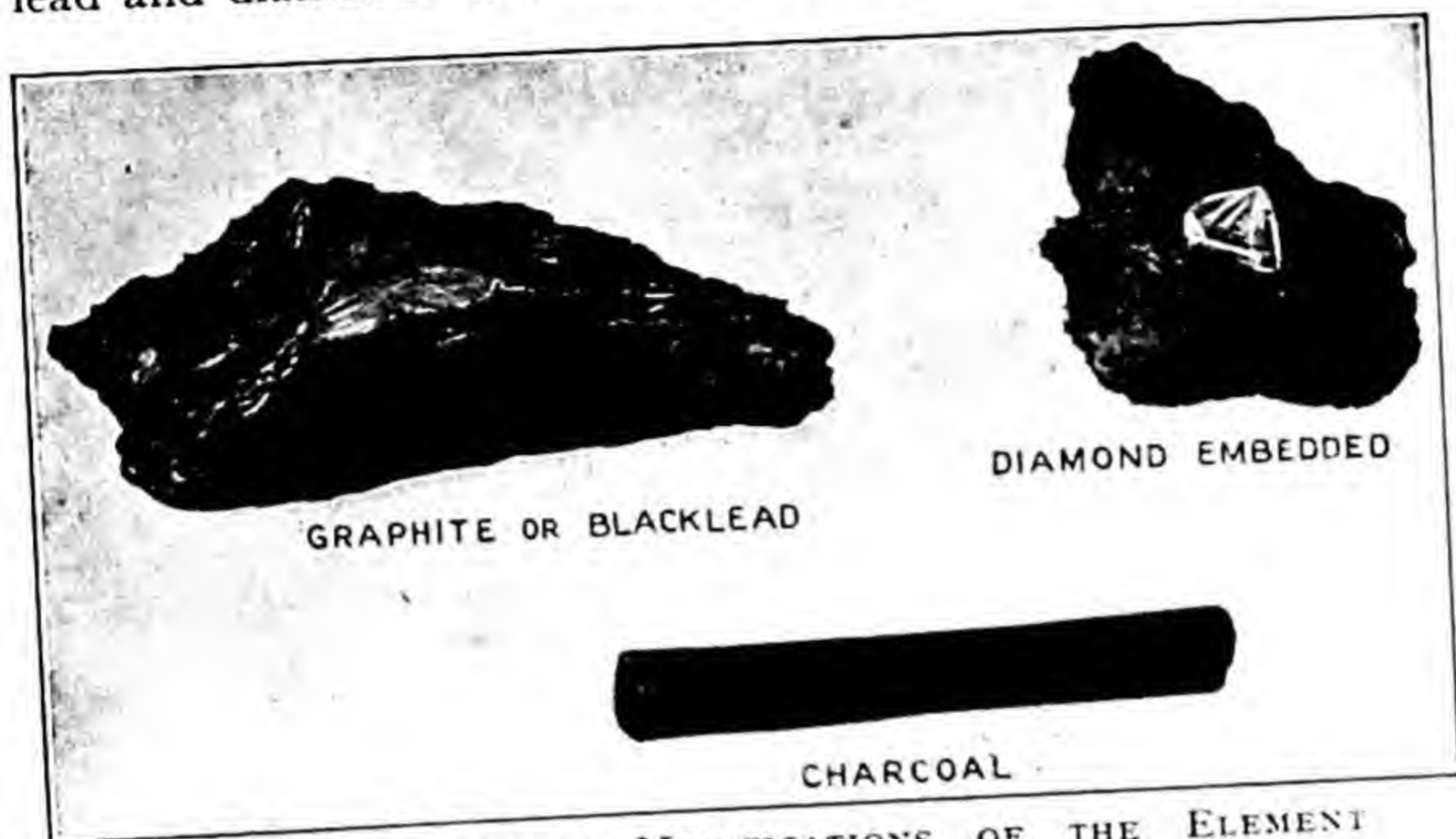


FIG. 59.—ALLOTROPIC MODIFICATIONS OF THE ELEMENT CARBON.

metal tin exists in two forms: the well known bright metallic form and a grey powder which is produced from white tin when



FIG. 60.—MEDAL SHOWING ATTACK BY 'TIN-DISEASE' CAUSED BY CONVERSION OF WHITE INTO GREY TIN, AN ALLOTROPIC FORM PRODUCED SLOWLY AT TEMPERATURES BELOW  $18^{\circ}\text{C}$ .

it is exposed to cold. Many old tin objects in museums have suffered from this change of white tin into grey tin (Fig. 60),

which goes on very slowly even at room temperature but more rapidly when the tin is strongly cooled. Aristotle (384-322 B.C.) said that tin 'melts' when exposed to cold, and he no doubt refers to this change. The grey form is really the one which is stable at cool room temperature (below  $18^{\circ}\text{C.}$ ).

It must be noted that isomeric change is an example of chemical change in which the substances neither increase nor decrease in weight (p. 52).



## CHAPTER IV

### THE EARLY HISTORY OF CHEMISTRY

**The early history of chemistry.**—The present views on the chemical elements and on chemical compounds as formed from them in definite proportions, explained in Chapter III, were reached only after centuries of work. The definition of an element which has been given dates from the seventeenth century, when Robert Boyle, in his *Sceptical Chymist* (1661), agreed to use 'elements and principles as terms equivalent, and to understand both by the one and the other, those primitive and simple bodies of which the mixed ones are composed, and into which they are ultimately resolved'. According to Boyle, therefore, the *elements* are *the practical limits of chemical analysis*, or are substances incapable of decomposition by chemical means. Boyle, however, although he showed experimentally that many things thought in his time to be elements were not so, was not able to give a list of true chemical elements. This was first done by Lavoisier, in his *Traité Élémentaire de Chimie* in 1789. Since his time, about ninety elements have come to be recognised, a list of which, with their symbols (p. 142), atomic weights (p. 138), and atomic numbers (p. 244), is given inside the front cover.

Until Boyle's time, the views on elements were not unlike those held in antiquity, when four elements, fire, air, water, and earth, were recognised by Aristotle. To these, the alchemists added three *principles*, mercury, sulphur, and salt. None of these were true elements in the sense understood by Boyle, since they were not true constituents of substances, and could not be separated from them by chemical processes.

**Theory of the four elements.**—The idea of an element occurs in the teachings of old Greek philosophers. Thales (640-546 B.C.) supposed all things were formed of water; Anaximenes (560-500 B.C.) of air; Herakleitos (536-470 B.C.) of fire; Empedokles (490-430 B.C.) of four 'roots', fire, air, water, and



ARISTOTLE, BY ROMAN BRONZE, 1027-1601.  
 COURTESY OF THE METROPOLITAN MUSEUM OF ART.

earth. Empedokles also taught attraction and repulsion. Aristotle (384-322 B.C.) adopted the four elements, but thought all things were made of a fifth, primary matter (*hulē*) on which a specific form (*eidos*) was imposed to produce a definite body, as a sculptor can make different statues from one block of marble. The form could be removed and replaced by a new one, so that the idea of the *transmutation of the elements* arose. Aristotle's



elements are really fundamental properties of matter, which he chose as hotness, coldness, moistness, and dryness, by combining which pair of opposites he obtained the four elements.

Water was a type of moist and cold things, fire of hot and dry, etc. A fifth immaterial element, the quintessence, was added later, corresponding with the ether. Such an expression as 'the fury of the elements', meaning air and water, still sometimes appears, but such literary phrases, based on worn-out scientific theories, are passing out of use.

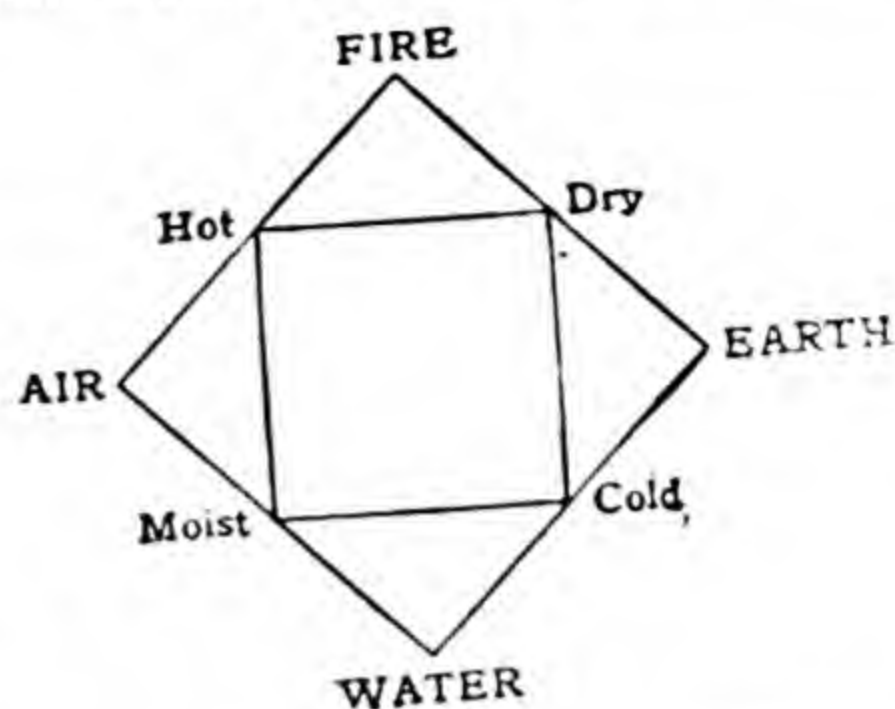


FIG. 62.—ARISTOTLE, 384-322 B.C.  
WHOSE THEORY OF THE ELEMENTS LASTED UNTIL THE TIME OF BOYLE.

Most of our common ideas and ways of looking at the world were really shaped by the old Greek philosophers, to whom we owe such concepts as matter, force, elements, number, space, time, etc.

**The earliest chemical knowledge.**—Several chemical substances, such as the oxides of copper, iron and zinc; alum; the sulphates of copper and iron; sulphides of arsenic and mercury, and vegetable and animal products, including dyes, were known in the Classical Period and, with some simple chemical operations such as the working of metal and alloys, gilding by means of solutions (amalgams) of gold in mercury, and testing gold and silver for purity, are described in the writings of Dioskurides (60 A.D.), Pliny the Elder (23-79 A.D., the author of the famous *History of Nature* in 37 books), and Galen (131-201 A.D., the great medical authority of antiquity). Even earlier than this we find Theophrastos (315 B.C.) describing some simple chemical operations, e.g., the manufacture of white lead (Greek, *psimuthion*): 'lead is placed in an earthen vessel over sharp vinegar, and after it has acquired some thickness of a kind of rust, which it commonly does in about ten days, they open the vessels and scrape it off. They then place the lead over the vinegar again, repeating over and over again the same process of scraping it till it is wholly gone. What has been scraped off they then beat to powder and boil [with water] for a long time, and what at last settles to the bottom of the vessel is white lead.' (*Treatise on Stones*.) This is a fairly accurate account of the process.

Pliny thus describes the preparation of mercury: 'They put vermilion in an earthen vessel well luted over with clay, upon which there is set a pan of iron, and the same covered over the head with another pot, well cemented. Under the earthen pot a good fire is made and kept continually blown. And thus by circulation there will appear a dew or sweat in the uppermost vessel, proceeding from the vapours set free. When this is wiped off it will be as liquid as water but in colour will resemble silver.' This description is imperfect and was no doubt copied by Pliny from an author he did not clearly understand.

We might have expected that such processes would have aroused the interest of learned men, and although they did in fact provide exercises in making up *theories*, only a few men seem to have made *experiments*, and the study of natural science was not held in high estimation in the Roman Empire,



with the exception of Egypt. There the more refined arts of working precious metals seem to have been cultivated in the temples either by the priests or, more probably, by special temple workmen, for a very long time, and the practical traditions handed down from one generation to another. A collection of Egyptian recipes of this type appears to form the contents of the famous **Papyrus of Leyden**, discovered in 1828 in a tomb at Thebes in Egypt, and kept in the Leyden Museum. Another part of the same papyrus was sent to Stockholm. The papyrus is written in Greek, its date is probably about 300 A.D. and it contains recipes probably copied from much older Egyptian sources. These deal mainly with the production of imitations of an alloy of gold and silver which is called by its old Egyptian name *asem* (the Greek *elektron* and Roman *electrum*), which was regarded as a separate metal, and with the preparation of alloys and plated objects which would 'serve for' the noble metals and were even 'better than the real' (an almost modern touch). There was no doubt in the mind of the writer that the imitations of noble metals, gems and expensive dyes were in no sense real. The Stockholm part of the papyrus (Fig. 64) deals also with gems and valuable dyes and their imitation. A quotation from the Leyden papyrus will illustrate the point of view:

'One powders up gold and lead into a powder as fine as flour, 2 parts of lead for 1 of gold, and having mixed them, works them up with gum. One covers a copper ring with the mixture; then heats. One repeats several times until the object has taken *the colour*. It is difficult to detect the fraud, since the touchstone gives the mark of true gold. The heat consumes the lead but not the gold.'

It is possible that the work represents the note-book of a fraudulent goldsmith.

**Alexandria.**—It is generally agreed that chemistry had its origin in Egypt, about the beginning of the Christian era, in the city of Alexandria founded by Alexander the Great at the mouth of the Nile in 331 B.C.

Here there were two famous libraries and the Museum or University. One of the libraries is said to have contained 700,000 books: it was accidentally destroyed by fire in 47 B.C. and the second was destroyed in 389 A.D. The Museum was a centre of learning in philology, philosophy, science, and medicine, and in the Roman period was very famous, the voyage to Alexandria to study in its schools being then regarded as essential to a medical man.

ΙΔ  
 ΜΗ  
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ΣΙΑΡΑΓΔΟΥ ΠΟΙΗΣΙΣ  
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Because of its composite population of Egyptians, Greeks, Jews, and other races, Alexandria was a centre for the blending of various cultures. It was essentially a Greek city, but Greek learning there came in contact with Eastern ideas. Greek philosophy, from the beginning of the Christian era, was changed at Alexandria into new systems, one of which was Neo-Platonism. The Eastern element became more prominent, and philosophy later sunk into occultism and magic, the corresponding change in religion giving rise to Gnosticism. These beliefs influenced the development of science, particularly of early chemistry or alchemy.

Alchemy arose in Alexandria about the beginning of the Christian era from the fusion of two streams of knowledge. One of these comprised the ancient Egyptian arts of metallurgy, dyeing and making coloured glass and imitation gems; this formed its practical part. The other, the theory, came from Greek philosophy, particularly the views of Aristotle on the primary matter (p. 60). It came to be believed that real gold could be produced by first divesting a common metal of its specific form (*eidos*) and giving it the form of gold. This process was brought about by the 'divine' or 'sacred' art, said to have been revealed to mortals by angels or the god Hermes Trismegistos, a form of the ancient Egyptian god of learning, Thoth, and hence alchemy was also called the 'Hermetic art'. The name of Hermes is preserved in the expression 'hermetically sealed' ('Hermes his seal,' in old books) for closing a glass vessel by melting the neck.

**The beginning of chemistry.** Up to the commencement of the Christian era we find no indication of the existence of chemistry in Europe or the Nearer East. Chemical operations were known to technical workmen, as we have seen, but the information was empirical. The name first occurs in an edict of the Emperor Diocletianus in 196 A.D., where the books of the Egyptians (in Alexandria) on *chemeia* are ordered to be burnt. The word appears in the Greek authors who report this as *χημεία*, but it is not a Greek word and appears to have been derived from the native designation of Egypt, a country which Plutarch, in his treatise *On Isis and Osiris*, written about 100 A.D., says was called *chemia* on account of the black colour of its soil. This statement is confirmed by the Egyptian inscriptions, where the hieroglyphic form of the word is used. The name probably meant 'the Egyptian art.' It occurs also in a Greek manuscript now at St. Mark's in Venice, copied



about 950 A.D. from a work of the Egyptian chemist, Zosimos of Panopolis, written about 250-300 A.D.

The earliest chemical books were written in Greek in the first four centuries A.D. The oldest actual manuscript is the one at St. Mark's in Venice, and there are many later ones in the Bibliothèque Nationale in Paris (see p. 68). The earliest author is probably Demokritos, not the old Greek philosopher of Abdera, the founder of the atomic theory (p. 135), but a writer of the first century A.D. Another old author is Mary the Jewess, who invented apparatus for distillation (the *ambix*), and for sublimation (the *kerotakis*), shown in Fig. 64.

The distillation apparatus, later called an *alembic* (Arabic *al ambiq*), had a lower vessel or *lopas* (afterwards called a *cucurbit* or *aludel*), and an upper part or *ambix*, this being the name of a cup with a long spout, which when inverted was very like the head of the apparatus as described and illustrated in the manuscripts. The sublimation apparatus, or *kerotakis*, comprised a small charcoal brazier, above which was a metal plate with cup-shaped depressions into which the material to be heated was put, and inverted over this was a glass bell-jar to receive the sublimate. The plate was like the metal palette used by painters using wax pigments for encaustic painting.

The treatises contain many technical terms not found in our Greek dictionaries, just as modern English text books on science contain many words not found in the dictionaries based on literary works. They also contain many common words used with very uncommon meanings, a favourite device of the later alchemists for concealing information. Zosimos, for example, speaks of a 'divine water', also called the 'bile of the serpent', which was made by boiling sulphur with milk of lime, and was a yellow solution of calcium polysulphide. This had the property of changing the colours of many metals, like lead and copper, and of giving coloured precipitates with solutions of metal salts. When mixed with vinegar, it formed a milky-white precipitate of sulphur, and a strong smell of sulphuretted hydrogen—Zosimos, in fact, says the operator should hold the nose when working with it.

The treatises also contain some obscure and mystical matter, and descriptions of visions, which seem to describe chemical operations in vague allegories. This style of writing has always been a feature of works on alchemy of all periods. The metals are denoted by the symbols of the planets with which they were associated, and there are symbols for apparatus and pre-



parations (pp. 139-140). The picture of a serpent eating its tail (the *ouroboros* symbol) perhaps denoted the unity of matter.

The treatises, however, contain a fair amount of practical chemical information, which appears in them for the first time, and also many diagrams of chemical apparatus (Fig. 64). The operations of fusion, calcination, solution, filtration, crystallisation, sublimation and especially distillation are all used and described, and methods of heating include the open fire, lamps, and the sand and water baths. Nearly all this practical knowledge has been ascribed to the Arabs, who really derived it from the very source we are now considering. The Arabic name *alchemy* is merely the Alexandrian-Greek *chemeia* with the Arabic definite article *al* prefixed.

An important feature of the Alexandrian treatises is that the fraudulent processes described in the Papyrus of Leyden have now become real **transmutations** of base metals into gold. The process was to be effected by 'changing the colour' of lead or mercury by means of various chemicals, and copper turned white by arsenic was regarded as a kind of silver. The transmuting agent (*xerion*) was called by the Arabs *aliksir* (elixir) and by the European alchemists the *philosophers' stone*, or the *tincture* (*i.e.* an agent to change the colour).

**Chemistry in Arabia.**—Soon after the death of Muhammad in 632 A.D., the Arabs had conquered much of Syria, Babylonia, Egypt, North Africa, and Spain. Their language spread, and their contact with the remains of the late Greek (or Hellenistic) culture enlarged their interests. The Greek capital, Byzantium (Constantinople), they never captured; this was first achieved by the Turks in 1453, and the fugitive Greeks took manuscripts to various parts of Europe, including those on alchemy, which then became known. Some of them were published in Latin translations in 1572 (see Fig. 65, where the date 1573 is an alteration). The Arabic caliphs were mostly patrons of learning, and the courts in the conquered lands became centres of intellectual activity. Greek works on philosophy, medicine, and alchemy were translated, first into Syriac (*i.e.* theological Aramaic), made by non-Arabs, particularly by Nestorian Christians—a sect which, cut off from the body of the Church of Alexandria for what was considered as heresy, was especially active in spreading a knowledge of the sciences to the Nearer East, and even to China. It has been said that, through the new city of Bagdad, founded in 762, 'a great stream of Greek and other ancient learning began to pour into the Muhammadan world and clothe itself in an

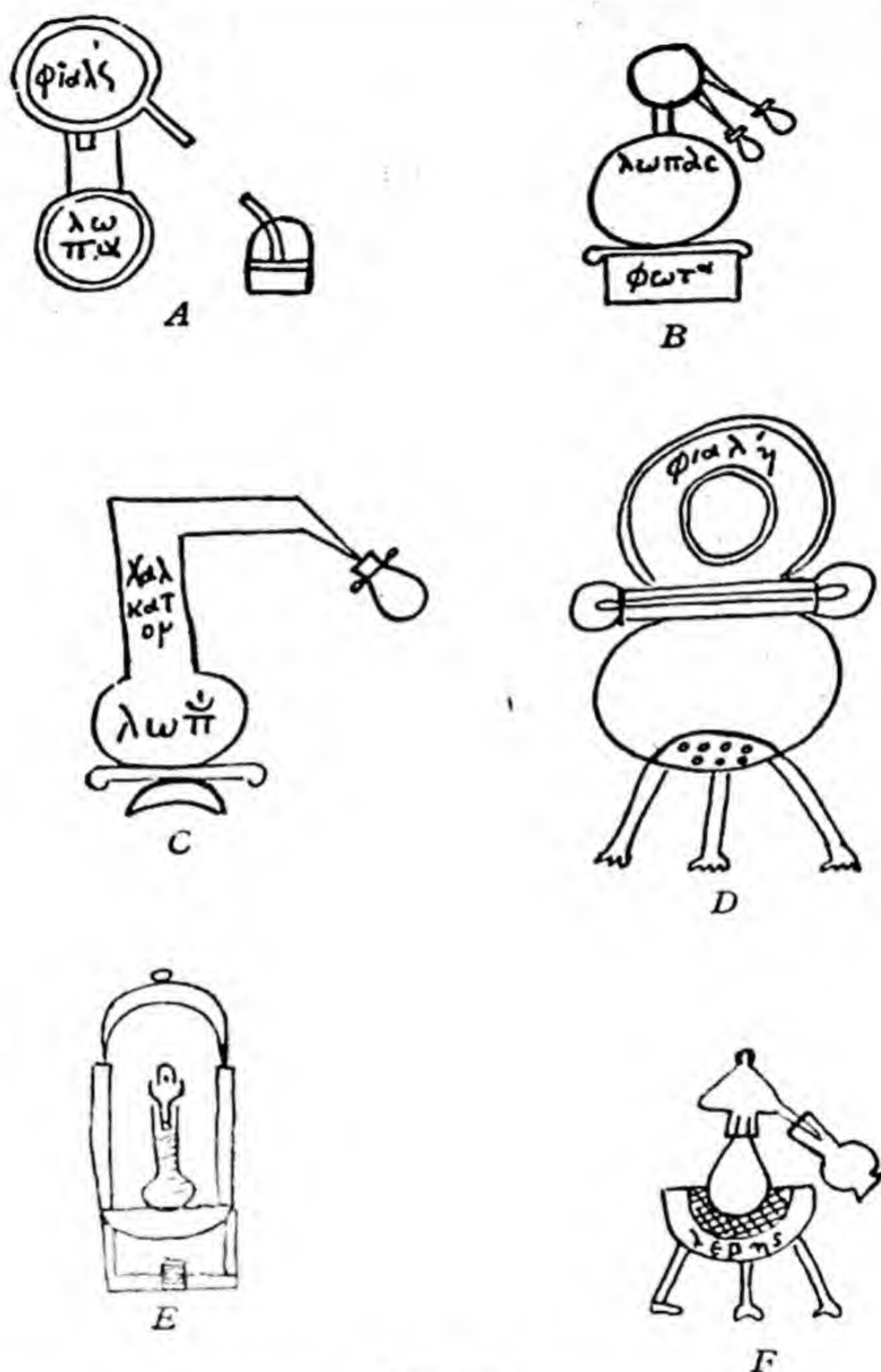


FIG. 64.

ILLUSTRATIONS OF CHEMICAL APPARATUS COPIED FROM GREEK MSS. OF ZOSIMOS AND OTHERS IN THE *Bibliothèque Nationale*, PARIS. THE GREEK NAMES OF THE APPARATUS WILL NOT BE FOUND IN THE DICTIONARIES. A, B, C AND F REPRESENT APPARATUS FOR DISTILLATION, later called ALEMBICS: IN THE MSS. THE LOWER PART IS CALLED *λωπας*, THE COPPER *phiale*. THESE ARE SOMETIMES HEATED BY LAMP (as in F), SOMETIMES ON A SAND BATH (as in E). D IS A KEROTAKIS, E AN APPARATUS FOR HEATING A PHIAL IN A SAND BATH, C IS A COPPER STILL. ALL THIS APPARATUS WAS WELL KNOWN BEFORE 300 A.D.



Arabic dress.' Some Syriac translations of Greek alchemical works still exist (see Fig. 66, and compare with Fig. 64).

By this time, alchemy had been known in Egypt for more than five hundred years, but a knowledge of it first reached Europe in Latin translations of Arabic works, mostly made in Spain from about 1100 A.D., so that for a long time it was thought that alchemy originated among the Arabs. Some Latin works of rather late date, *e.g.* those attributed to Geber, were also at one time thought to be translations of (unknown) Arabic works.

Chemistry among the Arabs was especially cultivated by Jābir ibn Hāyyan (720-813), who was thought to be the author of the works of Geber, and al-Rāzī or Rhases (866-925) a Persian, best known as a physician. The Arabic works of Jābir, which contain some practical material, but also much mystical, have recently been supposed to have been composed about a century after his death by an unknown author. The alchemical work of al-Rāzī, the *Secret of Secrets*, contains much practical information, but is quite different from his authentic medical works.

The physician ibn Sina or Avicenna (980-1036), born at Bokhara, passed as the author of a work on alchemy, *de Anima*, which was studied by Roger Bacon, but this is now supposed to have been compiled in Spain after Avicenna's death. In his authentic works, Avicenna is a critic of alchemy, which he thought was fraudulent.

A theory taught by Arabic authors, and attributed to Jābir, is that metals are composed of mercury and sulphur, and are generated from these in the interior of the earth, perhaps under

DEMOCRITVS

A. B. D. E. R. I. T. A

*Lib. de arte*

*Thos. Howell* M. A. G. N. A.

*Sive de rebus naturalibus.*

Nec non Synesii, & Pelagii, & Stephani Alexandrini, & Michaelis Pscl. in eundem commentaria.

Dominico Pizimentio Vibonensi Interprete.



PATAVINO  
Apud Simonem Galignanum  
M D LXXIII.

1771.

FIG. 65.—TITLE PAGE OF THE LATIN TRANSLATION OF GREEK ALCHEMICAL WORKS.

the influence of the corresponding planets. This theory seems to have been derived from some passages in Aristotle's *Meteorology*. It appears in an encyclopaedia written about 950 A.D. by the members of a secret society, the Brethren of Purity, at Basra,

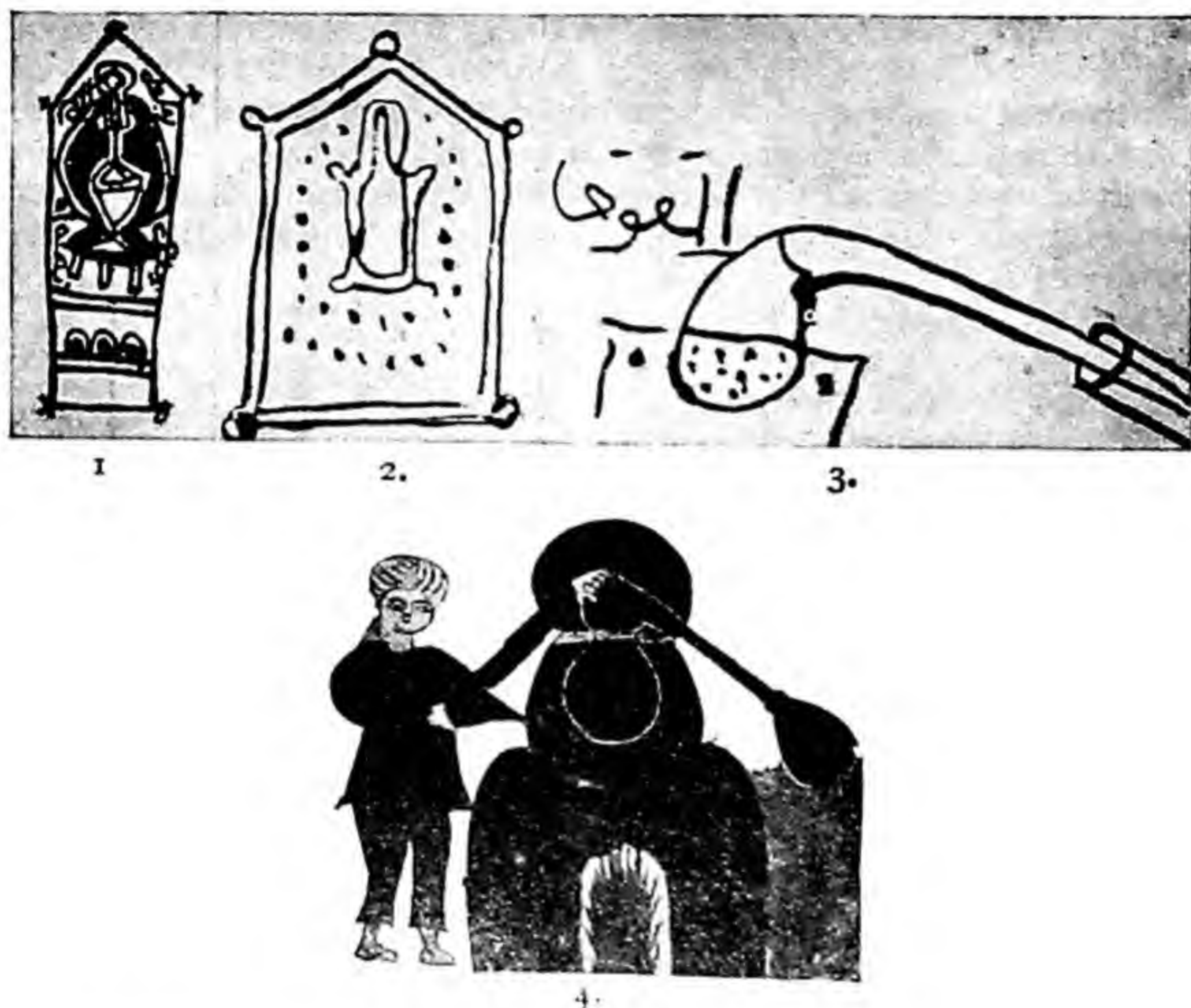


FIG. 66.

- (1) APPARATUS FOR DISTILLATION. (Syriac MS.)  
 (2) APPARATUS FOR DISTILLATION IN SMALL CHAMBER. (Syriac MS.)  
 (3) RETORT AND STILL. (Syriac MS.) A later addition.  
 (4) A STILL APPARATUS FROM A PAGE OF A FAIRLY MODERN ARABIC CHEMICAL MS. IN THE BRITISH MUSEUM.

which is largely compiled from Syriac translations made by earlier Nestorian Christians and based on Greek sources.

The sulphur and mercury of the alchemists were not the actual elements now known by these names, but 'principles' of the same kind as Aristotle's four elements. Mercury was the cause of metallic properties, such as density, lustre, and fusibility, whilst sulphur produced the colour and alterability by fire. The different metals were supposed to contain mercury and sulphur in



varying degrees of purity and 'fixity', those in gold and silver being the purest kinds.

Information from Mesopotamia, Persia, and even China, was incorporated into later Arabic alchemy, perhaps by way of Harran, the home of a heathen sect called the Sabeans, who kept alive the old Babylonian astrology and the belief in the relation of the metals and the planets.

The actual contributions of Arabic-writing authors to alchemy are very difficult to assess, but they were responsible for much less than was once believed. They did, however, serve in the transmission of a knowledge of alchemy to Europe, as will be seen.

**Hindu chemistry.**—After Alexander's penetration into India in 327 B.C., a knowledge of India reached the Greeks, and in the Roman period Indian wares reached Alexandria by sea. A study of Indian science is made very difficult by the lack of reliable dates for the earlier periods, so that it is not known how much is due to other nations, such as the Greeks. Some of the philosophical systems, such as the Upanishads and the Samkhya system, resemble Neo-Platonism. The atomic theory seems to have been known at a fairly early date. Although it is attributed to a philosopher Kanāda, about whom nothing is known, it first appears in some detail in the works of Buddhists and Jains (a related religious sect). It was well known in the fifth century A.D. The Hindu atomic theory differs in many ways from that of the Greeks, and may have been original; it recognises groups of small numbers of atoms, which we now call molecules.

Early Hindu pharmacy is represented by the Bower Manuscript of the fourth century A.D., in which only vegetable drugs are described. The later medical works *Susruta* and *Caraka*, perhaps of the eighth and ninth centuries A.D., describe solid caustic potash and soda (which are distinguished), the 'rusts' (oxides) of metals, and some metallic salts such as iron and copper vitriols. The use of mercury and mercury preparations in medicine seems to date from the eighth century, when Buddhism underwent a

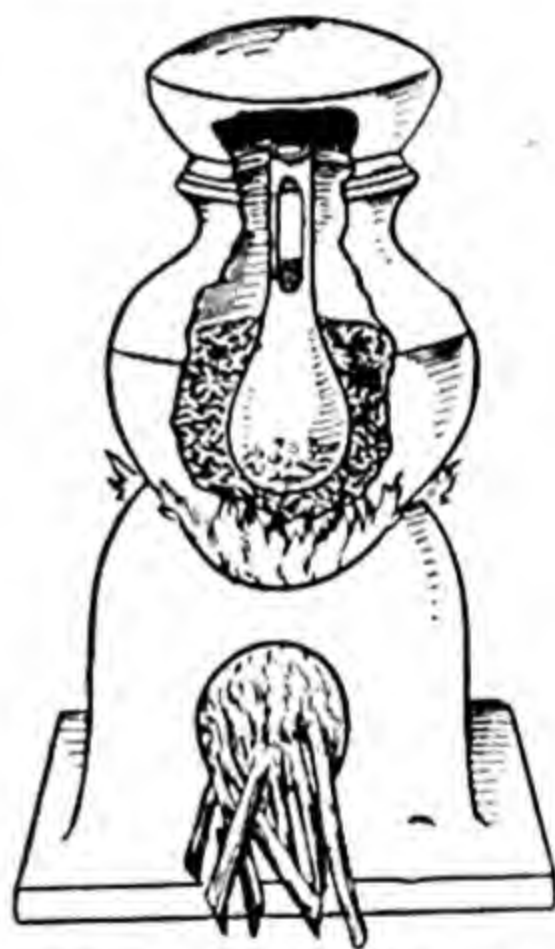


FIG. 67.—APPARATUS FROM INDIAN CHEMICAL MANUSCRIPT.



profound change into the so-called Tantra system, in which revivals of old religions were associated with magic and sorcery. A special philosophy, called the Mercury System, arose.

An early Hindu alchemist is Nāgārjuna, perhaps about 850 A.D. The later alchemical works are of very uncertain date, and the mineral acids are mentioned only in the sixteenth century. Although it has been suggested that Hindu alchemy borrowed from the Arabs, this is uncertain.

In his book on India, Albiruni (973-1048) says, in a chapter called: "On Hindu Sciences which prey on the Ignorance of the People", that he could get very little information about alchemy and alchemists, and adds: "I only heard them speaking of the processes of sublimation, calcination, analysis, and the waxing of talc (which they call in their language *talaka*), and so I guess that they incline towards the mineralogical method of alchemy."

The contributions of Hindu scholars to mathematics seem to have been more important than their chemistry.

**Chemistry in China.**—Although the dates in Chinese history are more reliable than those for India, the authenticity of some earlier books has been called into question. It seems likely, however, that alchemy appeared in China at least as early as in Egypt, and arose independently. There is, however, evidence of a relation between Alexandria and China about the beginning of the Christian era.

The earliest 'scientific' book in China is the *Yi-king* (*king* means book), or 'canonical book of changes', dealing with the ever-changing events of nature and experience, which is ascribed to Wen Wang (1200 B.C.), and is probably complete and authentic. The 'text' consists only of arrangements of long and short lines, and its contents depend upon interpretation. It is supposed to describe the two principles of *yin* and *yang*, which are female and male, dark and light, cold and warm, even and odd, etc.; they are cosmic forces, the origins of all being, and supposed to be in constant relation.

The *Shu-king*, or 'canonical book of records' is regarded as authentic. In a part which may be as old as 2200 B.C., there is a description of the Chinese *five elements*, which are: fire, water, wood, metal, and earth, 'which move and revolve between heaven and earth without ever ceasing', i.e. undergo unceasing cycles of change. These are different from the Greek four elements: fire, air, water, and earth, a knowledge of which first reached China with Buddhism from India. Buddhism was



'officially' introduced from India in the time of Ming-ti, 58-75 A.D.

The Chinese had an early knowledge of metals, including copper, bronze, brass, and iron. In later works there is a description of the extraction of zinc from the ore by heating with coal in crucibles (Fig. 68), without distillation. The mercury ore cinnabar ( $\text{HgS}$ ) occurs in China, and the extraction of mercury,

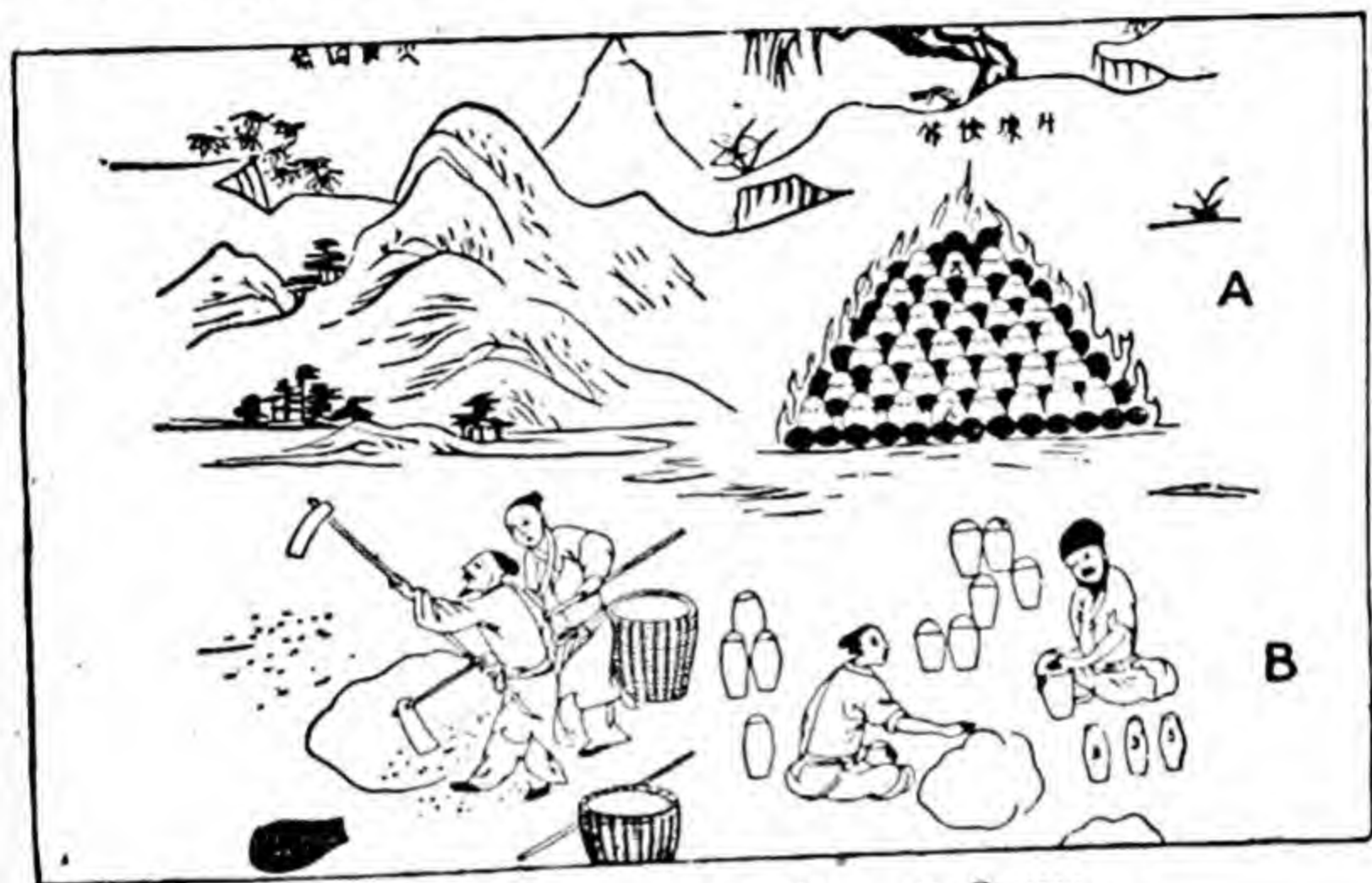


FIG. 68.—EXTRACTION OF ZINC IN CHINA.

(A) 'MEILER' OF SUPERPOSED CRUCIBLES SURROUNDED BY COAL. (B) FILLING AND LUTING THE CRUCIBLES. THE METAL IS NOT DISTILLED AND THE PROCESS RESEMBLES THAT DESCRIBED BY STRABO (64 B.C.-24 A.D.).

and the formation of artificial cinnabar by subliming mercury and sulphur, were known fairly early. True porcelain was made about 600 A.D., much earlier than in the West.

Alchemy appeared with later Taoism, a philosophy of Lao-Tsze (born 604 B.C.). The *tao* (a word with many meanings) at first meant 'the first and last cause of existence'. All things are formed from it, and all return to it, in cycles. A life based on Taoism could be prolonged. Taoism changed (like the Buddhist Tantra) into magic and occultism from the time of Liu Nan, or Hoai-nan-tsze, a prince of the court of the Emperor Wu-ti (140-86 B.C.), which was frequented by makers of the *tan*, or elixir of life, which would enable its possessor to prevent death, to rise to heaven, to assume other forms, and to work miracles.

The most celebrated alchemist of China was the Taoist Ko-hung, or Pao-po-tsze, in the fourth century A.D., who wrote several treatises on alchemy which are extant. His ideas are said to show a close resemblance to the Yogi system of India, which consists in stopping the pulse, heart beats, and some other physiological processes, by will power. He was chiefly concerned with the elixir of long life, the *kin tan*, by taking which, and gold, the body is preserved from decay. When vegetable matter is burnt it becomes ashes, but when the *tan sha* (cinnabar) is subjected to heat it produces mercury. When it suffers further changes this becomes cinnabar again. Ko-hung says that if the *tan* be placed over a hot fire, 'gold will be instantaneously produced; the production of gold is a sign of the completion of the elixir.' No complete Chinese text on alchemy has ever been translated and the subject, although of considerable interest, is very imperfectly known.

**Alchemy in Europe.**—The Greek treatises on the 'divine art,' which contain the beginnings of chemistry, were unknown in Europe during the middle ages, and the information on alchemy arrived with translations of Arabic works made in Spain—the point of contact of the Muslim and European cultures, and the principal focus for the transmission of Arabic learning to Europe. The usual method of translation, we are told, was for an Arabic text to be taken to Toledo, where it was read out in Spanish by a baptised Jew or Moor, and his version taken down in Latin. These versions (or 'perversions' as they have been called) began to appear about 1100 A.D. and some of the great scholastic minds became interested in the subject of alchemy. Albertus Magnus (1193-1260) wrote a clear and concise treatise on alchemy and an account of metals and minerals. He soon found that alchemy was a pretended science: alchemical gold, he says, after six or seven trials by fire, is turned into a powder.

Roger Bacon (1214-1292), who relied mainly on Avicenna, wrote treatises on the subject in which the theories are soberly and clearly summarised and the high-flown language of his Arabic sources is omitted. He was a profound believer in alchemy, but after the adverse criticism of Albertus Magnus, the great schoolmen seem to have lost interest in the subject, which was then cultivated mainly by crowds of fraudulent 'artists,' or 'adepts,' who wandered over Europe in search of wealthy patrons of their worthless art. Large numbers of books on alchemy were written in the period 1250-1500, mostly quite unintelligible and full of the most obscure jargon. The alchemist



appears in English literature with Chaucer (1400 A.D.), and is criticised acutely in Ben Jonson's play, *The Alchemist* (1610).

Experiments on the supposed transmutation included the roasting of the sub-metallic mineral galena in air, when lead was formed, with a strong smell of sulphur; and the production of a small button of silver when the lead was burnt off by heating on a cupel or dish made of bone-ash. Also, if iron pyrites, a yellow mineral looking somewhat like gold, was melted with lead, and the lead cupelled, a minute amount of gold was left.



FIG. 69.—ROGER BACON (?) WITH A PUPIL.

Both the silver and gold, of course, pre-existed in the minerals and are prepared from them at the present day. Again, a steel knife-blade dipped into a solution of blue vitriol (copper sulphate) apparently became converted into copper.

The later history of alchemy, however, is mainly that of fraud practised by the 'adepts' on credulous dupes. One method of effecting transmutation was to stir the materials in the crucible with a hollow iron rod filled with gold powder, and stopped with wax. Another deception was to take a nail, half of iron and half of gold, and cover it with some black substance. It was then dipped into a liquid and stirred, when the black was

washed away and the part of the nail which dipped in the liquid was apparently turned into gold.

There are several old accounts of transmutations supposed to have been carried out in the presence of witnesses of the highest reputation for honesty.



FIG. 70.—PARACELSUS, 1541. LEANING ON HIS SWORD,  
THE HILL OF GOLD AND SILVER.—A TALISMAN.

In 1925, Mieth in Germany and Nagaoaka in Japan, both experimenters of repute, claimed to have converted mercury into gold by means of an alchemical treatment, and the artificial production of gold has been the subject of patents. Other, equally reputable, experimenters have succeeded in repeating



the process, although the artificial transmutation of elements is now well-established (p. 255).

**Iatrochemistry.**—Although not one of the alchemists ever succeeded in transmuting a base metal into gold or in preparing the elixir of life, the great amount of work done with these ends in view bore fruit in other directions. In the sixteenth and



FIG. 71.—JOHANN BAPTISTA VAN HELMONT, 1577-1644  
HE BELONGED TO THE NOBILITY (HIS COATS OF ARMS ARE SEEN IN THE BACKGROUND) BUT DEVOTED HIS LIFE TO STUDY AND EXPERIMENT

seventeenth centuries another school of chemists arose, called the **Iatrochemists**, *i.e.*, the **medical chemists**, who attempted to prepare the **elixir of life**, which should cure all diseases, and confer perpetual youth. Paracelsus (1493-1541) was the founder of this sect; he believed in the philosopher's stone and the elixir of life. Paracelsus was a remarkable figure. He was essentially a reformer of medicine and in particular he opposed Galen and Avicenna, whose worn-out systems were still the mainstay of the physician. Paracelsus taught that the real

elements were mercury, sulphur and salt. We have an idealised account of him in Browning's poem. His pupil, Van Helmont (1577-1644), represents the beginning of the transition from alchemy to modern chemistry. His writings show some scientific method, although he still believed in transmutation, having seen the operation performed once by an adept, and sought for the *alkahest*, or universal solvent. He considered that all materials were derived from water, as taught by Thales (600 B.C.), and describes an experiment in which a small willow twig was grown in a weighed pot of earth, supplied only with water. After five years the tree was weighed, and had gained 164 lb. in weight, whereas the earth had lost practically nothing. Hence he concluded that the tree had been formed solely from water.

It is something of an irony of fate that this erroneous conclusion, in which the assimilation of carbon dioxide from the air by the plant was ignored, should have been reached by the discoverer of that gas. Van Helmont invented the name *gas*, derived from *chaos*, describing the supposed wild motion of its particles, and designated carbon dioxide as *gas sylvestre*, i.e., the 'gas of the woods,' or the 'wild, untamable gas,' because, having corked up limestone and acid in a bottle, he found that the latter was burst by the gas sylvestre. A gas, according to Van Helmont, is something which cannot be kept in a vessel. He mentioned another gas, *gas pingue*, which is inflammable, and is produced in fermentation. It was probably impure hydrogen.

**Robert Boyle.**—Modern chemistry may be said to have begun with Robert Boyle (1627-1691), and for two reasons. In the first place Boyle was the first to study chemistry for its own sake, and not as a means of making gold or medicines. In the second place, he introduced a rigorous experimental method into chemistry, and in particular overthrew the doctrines of the Aristotelian and alchemical elements, by showing that none of them could by any process be extracted from metals. In the case of gold, neither water nor solvents can extract sulphur or mercury from it: 'the metal may be added to, and so brought into solution or crystalline compounds, but the gold particles are present all the time, and the metal may be reduced to the same weight of yellow, malleable, ponderous substance as it was before the experiment.'

An element, according to Boyle, is some kind of matter which cannot by any known means be resolved into two or more simpler substances (p. 52).



Boyle was a good experimenter and improved much of the apparatus in use in his time. He made many experiments on the effect of reduced pressure by means of the air pump (p. 51) and among other things he describes distillation under reduced pressure and the apparatus for carrying out the process (Fig. 72). The *Sceptical Chymist*, one of Boyle's works which appeared in 1661 and has been reprinted in the *Everyman's Library*,

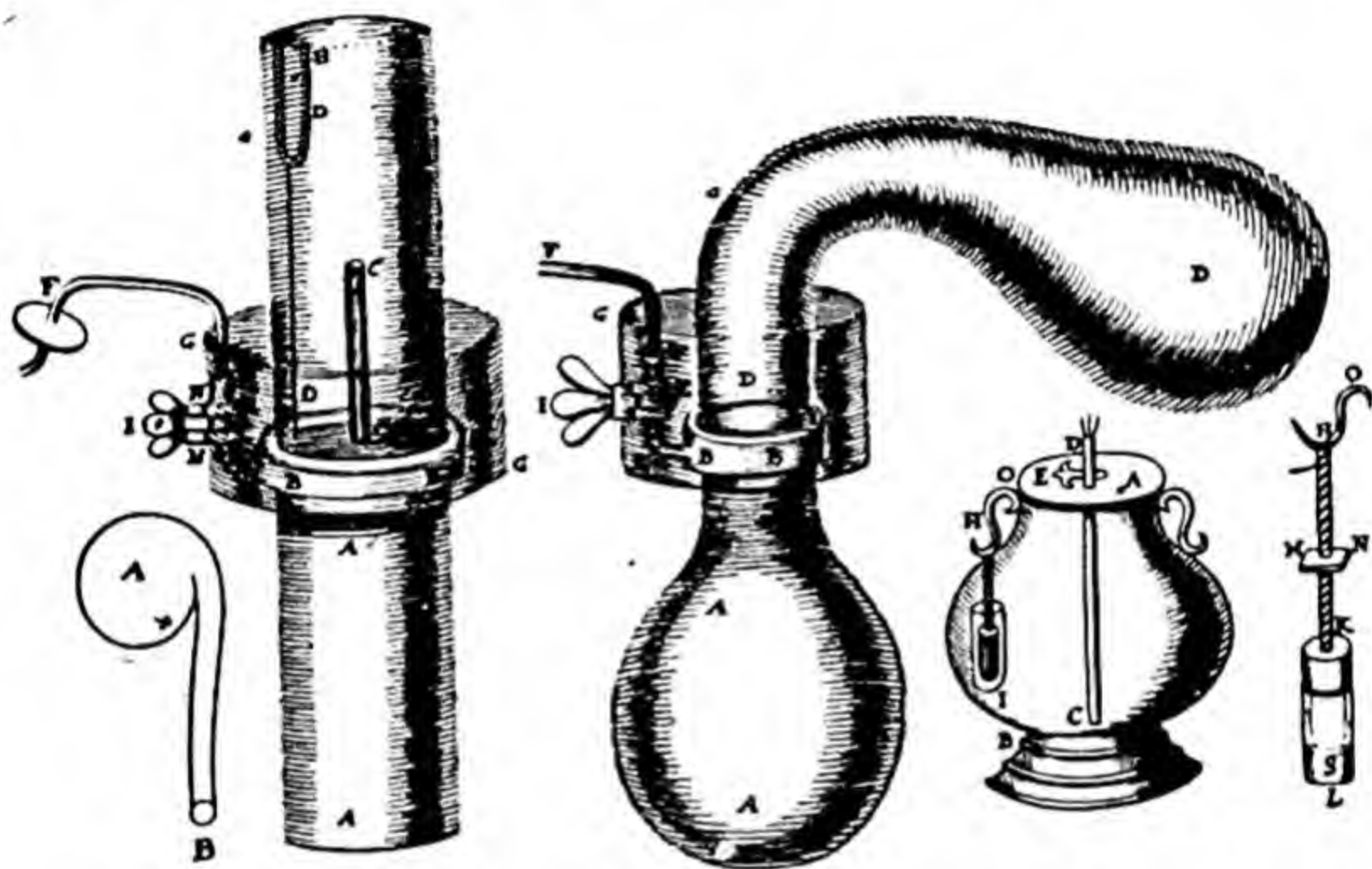


FIG. 72.—APPARATUS FOR DISTILLATION UNDER REDUCED PRESSURE, ETC.  
USED BY BOYLE.

contains his views on the elements but it does not give an adequate impression of his experimental skill, for which his other works must be consulted.

**The chemical elements.**—About ninety elements have been discovered since Boyle's time, but many of these are very rare and scarcely ever seen even by chemists. About 98 per cent. of the crust of the earth, to a depth of ten miles, consists of compounds of only eight elements, and of these oxygen makes up nearly fifty per cent.

In the ocean, oxygen makes up eighty-six per cent. of the elements and hydrogen about eleven per cent. The sea also contains about two per cent. of chlorine, mainly in the form of sodium chloride (common salt). It has been assumed that the central core of the earth consists mostly of metallic iron with

some nickel, surrounded by a shell of sulphides and oxides of heavy metals, and this in turn by a layer of silicates. Another view considers the intermediate zone to consist principally of oxides. The temperature of the interior is supposed to be about  $1500^{\circ}\text{C}$ .; another estimate gives  $3000^{\circ}\text{C}$ .

The *principal* constituents of the crust of the earth are given below (H. S. Washington, 1920):

Oxygen	-	46.43	Remaining	
Silicon	-	27.77	elements	- 1.37
Aluminium	-	8.14	including:	
Iron	-	5.12	Titanium	- 0.629
Calcium	-	3.63	Phosphorus	- 0.130
Sodium	-	2.85	Hydrogen	- 0.127
Potassium	-	2.60	Manganese	- 0.096
Magnesium	-	2.09	Fluorine	- 0.077
		<hr/>	Chlorine	- 0.055
		98.63	Sulphur	- 0.052
			Carbon	- 0.027

The great pressures in the interior of the earth would raise the melting points of the materials by about  $50^{\circ}\text{C}$ .

Living things consist principally of oxygen, carbon, hydrogen, nitrogen, sulphur, calcium and phosphorus—the last two occur in the form of calcium phosphate in bones, but some phosphorus compounds are present in the tissues.

If we include the air, the sea and other waters, and the crust of the earth to a depth of twenty-four miles in making an estimate of the occurrence of the elements, we obtain the following table, due to F. W. Clarke:

Oxygen	-	49.85	Calcium	-	3.18	Hydrogen	-	0.97
Silicon	-	26.03	Sodium	-	2.33	Titanium	-	0.41
Aluminium	-	7.28	Potassium	-	2.33	Chlorine	-	0.20
Iron	-	4.12	Magnesium	-	2.11	Carbon	-	0.19

This distribution is shown graphically in Fig. 73.

The proportion of hydrogen has increased, as compared with that in the former table, on account of the inclusion of the water, but the amount of carbon, which may be taken to include great masses of rocks such as limestone and dolomite, is still very small and thus the share of living animals and plants in making up the composition of the earth is almost insignificant. It will be noticed that titanium, which is commonly called a 'rare element,' is much more abundant than carbon and twice as



abundant as chlorine. The very small amounts of radioactive elements in the earth are supposed to be of importance in maintaining the temperature of the earth.

It is now believed that only two or three chemical elements remain to be discovered, since an enumeration of the elements is possible by the method of X-ray spectra (p. 244).

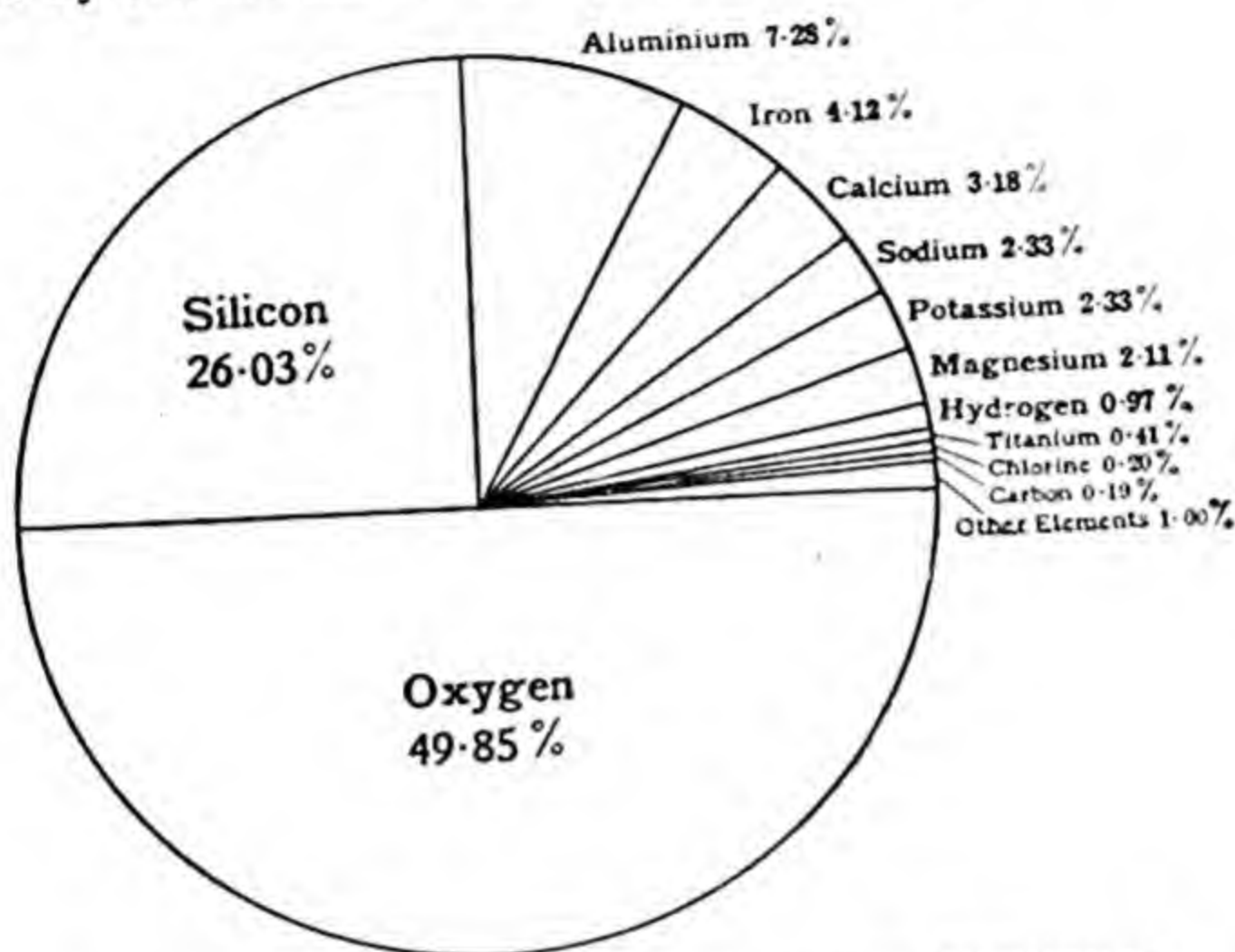


FIG. 73.—THE DISTRIBUTION OF THE ELEMENTS.

'The purpose of chemistry,' it has been said, 'seems to have changed much from time to time. At one time chemistry might have been called a theory of life, and at another time a department of metallurgy; at one time a study of combustion, and at another time an aid to medicine; at one time an attempt to define a single word, the word *element*, and at another time the quest for the unchanging basis of all phenomena. Chemistry has appeared to be sometimes a handicraft, sometimes a philosophy, sometimes a mystery, and sometimes a science.'

## SUMMARY OF THE EARLY HISTORY OF CHEMISTRY

140 B.C. Alchemy said to have begun in China.

0-50 A.D. The first treatises on the 'divine art' appeared in Alexandria, in Egypt, containing the earliest chemistry.

300 A.D. Ko Hung, the most celebrated Chinese alchemist.

- 300 A.D. Papyri of Leyden and Stockholm, summarising earlier technical information on metallurgy, dyeing, imitation of precious stones, etc.
- 300 A.D. Zosimos, in Egypt, describes many chemical operations : solution, filtration, fusion, sublimation, distillation, etc., and several chemical substances and reactions.
- 640 A.D. Egypt conquered by the Arabs, who later on caused translations by Nestorian Christians to be made of the Egyptian books on chemistry (which were written in Greek). The subject was especially studied by Jabir ibn Hayyan (800 A.D.), Rhases (*d.* 923 A.D.) and Avicenna (*b.* 980 A.D.). The idea that metals were composed of mercury and sulphur was introduced. Arabic chemistry is merely a continuation of that of Egypt.
- 800-900 A.D. Hindu chemistry resembled that of the Arabs.
- 1100 A.D. Alchemy appears in Europe by way of translations made in Spain from Arabic works. Roger Bacon and Albertus Magnus wrote on it about 1300.
- 1493-1541 A.D. Paracelsus, the founder of iatrochemistry, or chemistry applied to the service of medicine.
- 1577-1644 A.D. Van Helmont : he invented the name *gas* and described carbon dioxide as *gas sylvestre*.
- 1627-1691 A.D. Robert Boyle : the founder of modern chemistry : he defined a chemical element and made many experiments on combustion, etc.



## CHAPTER V

### THE COMPOSITION OF AIR AND THE THEORY OF COMBUSTION

**The discovery of gases.**—We can easily understand why the discovery of gases and the investigation of their properties were



FIG. 74.—STEPHEN HALES, 1677-1761.

rather late in the study of chemistry. We are now accustomed to have coal gas supplied to our houses, but this would have

been thought a wonderful thing by the early chemists. Van Helmont, who invented the name gas, about 1630, described two gases—*gas sylvestre* (carbon dioxide) and *gas pingue* (impure hydrogen, or perhaps marsh gas), but he was of the opinion that a gas cannot be contained in a vessel. Robert Boyle was probably the first to collect a gas. He filled a bottle with dilute sulphuric acid, put some iron nails in it, and inverted the bottle

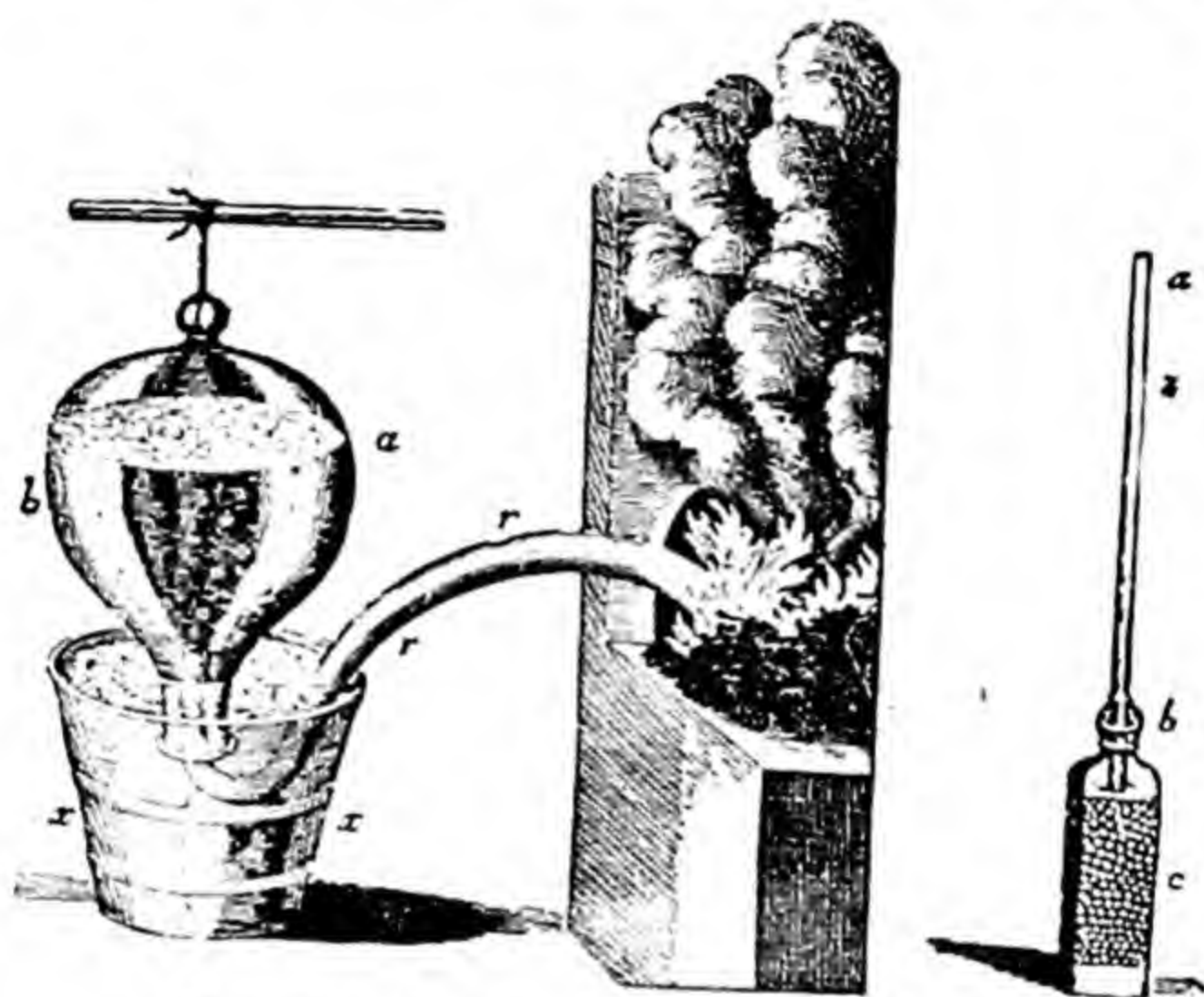


FIG. 75.—APPARATUS USED BY HALES.

ON THE LEFT IS THE GUN BARREL (r) HEATED IN A FIRE. THE GAS IS COLLECTED IN THE GLOBE (a) OVER WATER IN THE TUB (r). ON THE RIGHT IS A BOTTLE FILLED WITH FERMENTING PEAS OVER MERCURY. THE PRESSURE OF THE GAS EVOLVED DRIVES THE MERCURY INTO THE VERTICAL TUBE (ab), WHICH IS FIRMLY FIXED INTO THE BOTTLE AND DIPS INTO THE MERCURY IN THE LOWER PART.

in a dish of the acid. Bubbles of gas (hydrogen) rose from the iron and collected in the bottle. Boyle also knew that hydrogen was inflammable.

In 1727 the Rev. Stephen Hales, vicar of Teddington in Middlesex, published a remarkably interesting book called *Vegetable Staticks* in which he describes several experiments on gases. He heated various materials in a bent iron gun-barrel, and collected the gas evolved by allowing it to displace water from a large globe inverted in a tub of water (Fig. 75). With this apparatus he must have collected several gases, but he contented himself with measuring their volumes without



studying their properties and so missed the discovery of the individual gases.

The chemistry of gases really began with the work of Joseph Priestley, a nonconformist minister of Leeds who devoted his spare time to the study of science. His experiments were pub-



FIG. 76. — JOSEPH PRIESTLEY (1733-1804).

lished in six volumes of *Observations on Different Kinds of Air*, the first appearing in 1774. Priestley invented much of the apparatus used in the manipulation of gases, although it should be remembered that Cavendish in 1766 had published an account of some very careful experiments on two gases then known; carbon dioxide, which was called *fixed air*, and hydrogen, called *inflammable air*. Priestley discovered a number of new gases,

and in addition to collecting gases over water he showed that those which are very soluble in water, such as ammonia and sulphur dioxide, may be collected over mercury. Some of Priestley's apparatus is shown in Fig. 77, which is reproduced from a plate in his *Observations on Air*, and Fig. 78 shows part of his laboratory, reproduced from the same work.

In Fig. 77 we see the pneumatic trough *a*, with the shelf *bb*, filled with water in which stand the jars, *cc*, containing gases,

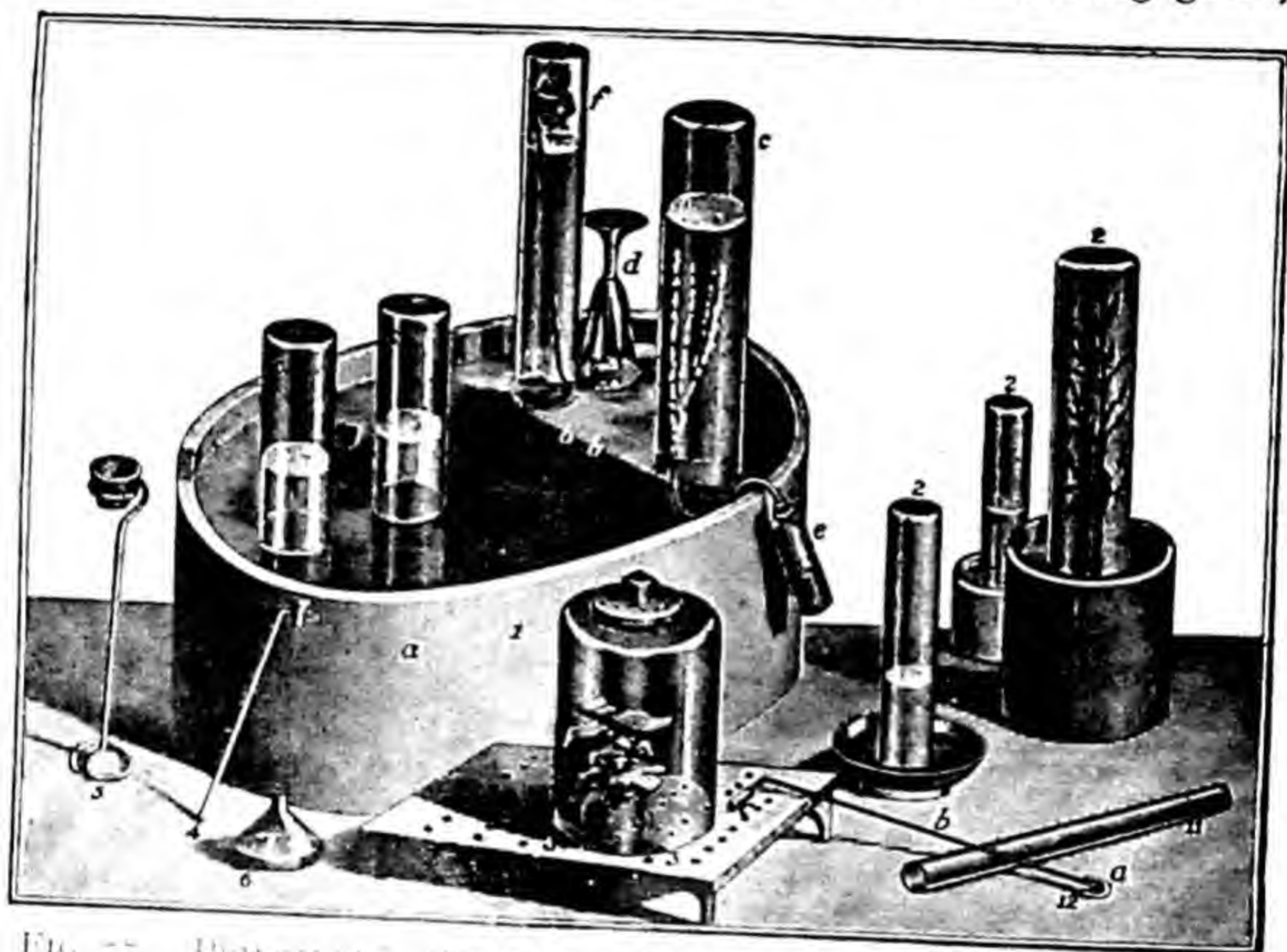


FIG. 77. PRIESTLEY'S PNEUMATIC TROUGH AND OTHER APPARATUS.

and another jar, *c*, is on the shelf receiving gas from the generating bottle, *c*. In the inverted glass, *d*, is a mouse, these animals being kept in the arrangement, *3*. The jar, *f*, contains a cup supported on a wire stand, also shown in *5*, in which a substance may be exposed to a gas. A plant growing in a gas is shown in *2*, and other apparatus for the manipulation of gases is depicted. In Fig. 78 we see a substance being heated in a gun-barrel in the fire and the gas evolved collected in a suspended pneumatic trough over mercury. A substance in the tube *8c* is heated by a candle and the gas, after passing through *d* to condense any liquid, is collected over mercury in *8d*. In *10* a gas evolved in



c is collected over water, passing through a bladder on the way so as to allow of the agitation of the bottle. (India-rubber tubing was then quite unknown.) Fig. 18 on the blackboard at the back is like a eudiometer but was filled with a liquid through which sparks were passed. Fig. 19 is the same as the apparatus used by Cavendish (see our Fig. 255).

**Experiments with gases.**—Gases are not so easily distinguished from one another as liquids and solids, and one of the most

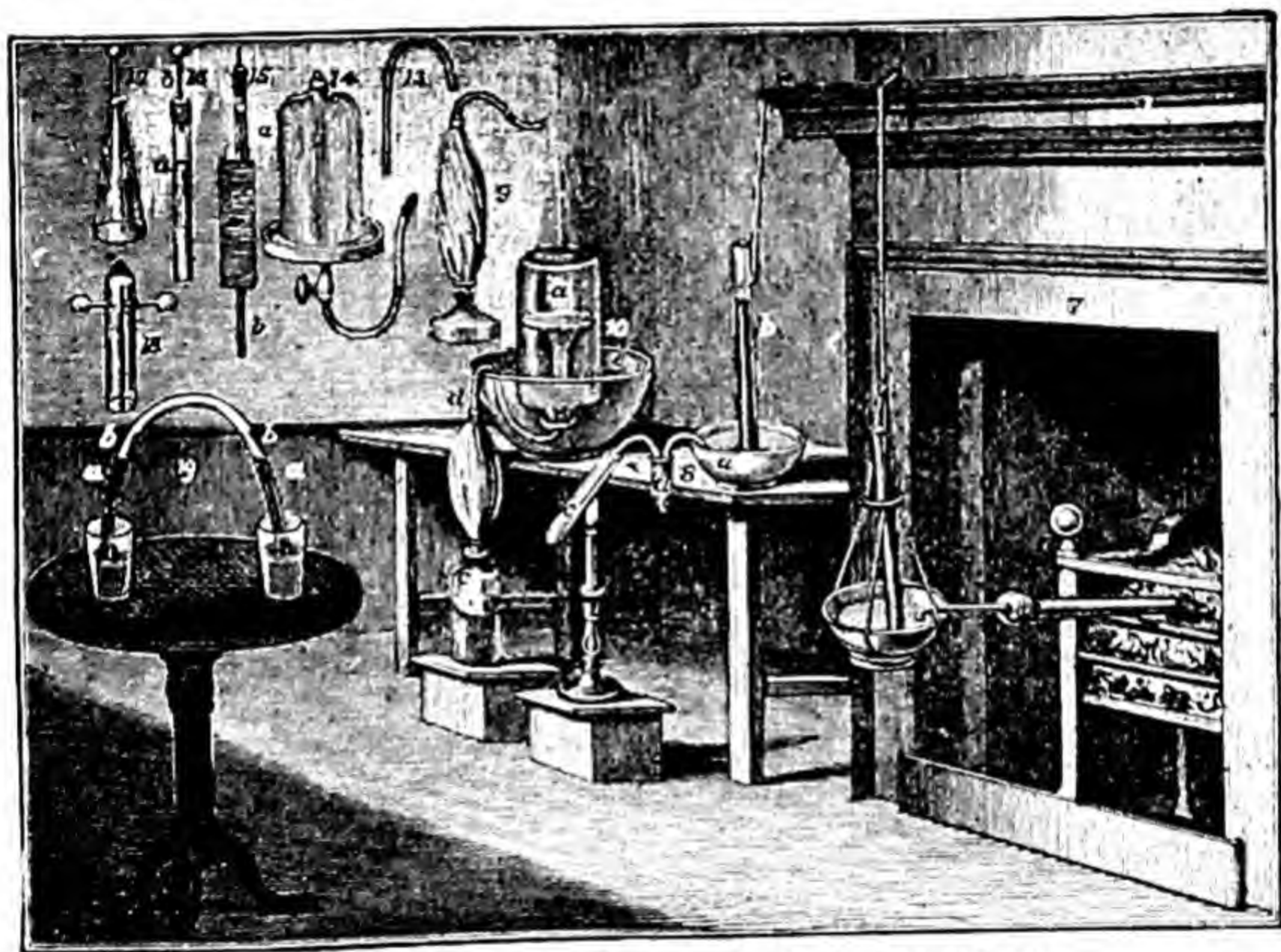


FIG. 78 — PART OF PRIESTLEY'S LABORATORY.

important parts of the study of chemistry is the acquisition of familiarity with various common gases. Let us suppose we are given glass jars containing the following gases: oxygen, hydrogen, chlorine, nitric oxide and carbon dioxide.

By simple *observation* it will be seen that chlorine has a greenish-yellow colour, whilst the other gases are colourless. These colourless gases may, however, be distinguished by appropriate *experiments*.

(1) The glass plates are removed from the jars so as to bring the gases in contact with the air. Nothing occurs except with the nitric oxide, which produces deep red fumes.

(2) A little lime water is poured into the other jars, and shaken. The lime water is unchanged in appearance in all the jars except that containing carbon dioxide, in which it becomes turbid and white.

(3) A lighted taper is inserted into each of a new set of jars of the gases. In oxygen it burns with a brilliant flame, in chlorine with a smoky red flame, but in the other jars it is extinguished. The hydrogen itself, however, takes fire and burns with a pale flame.

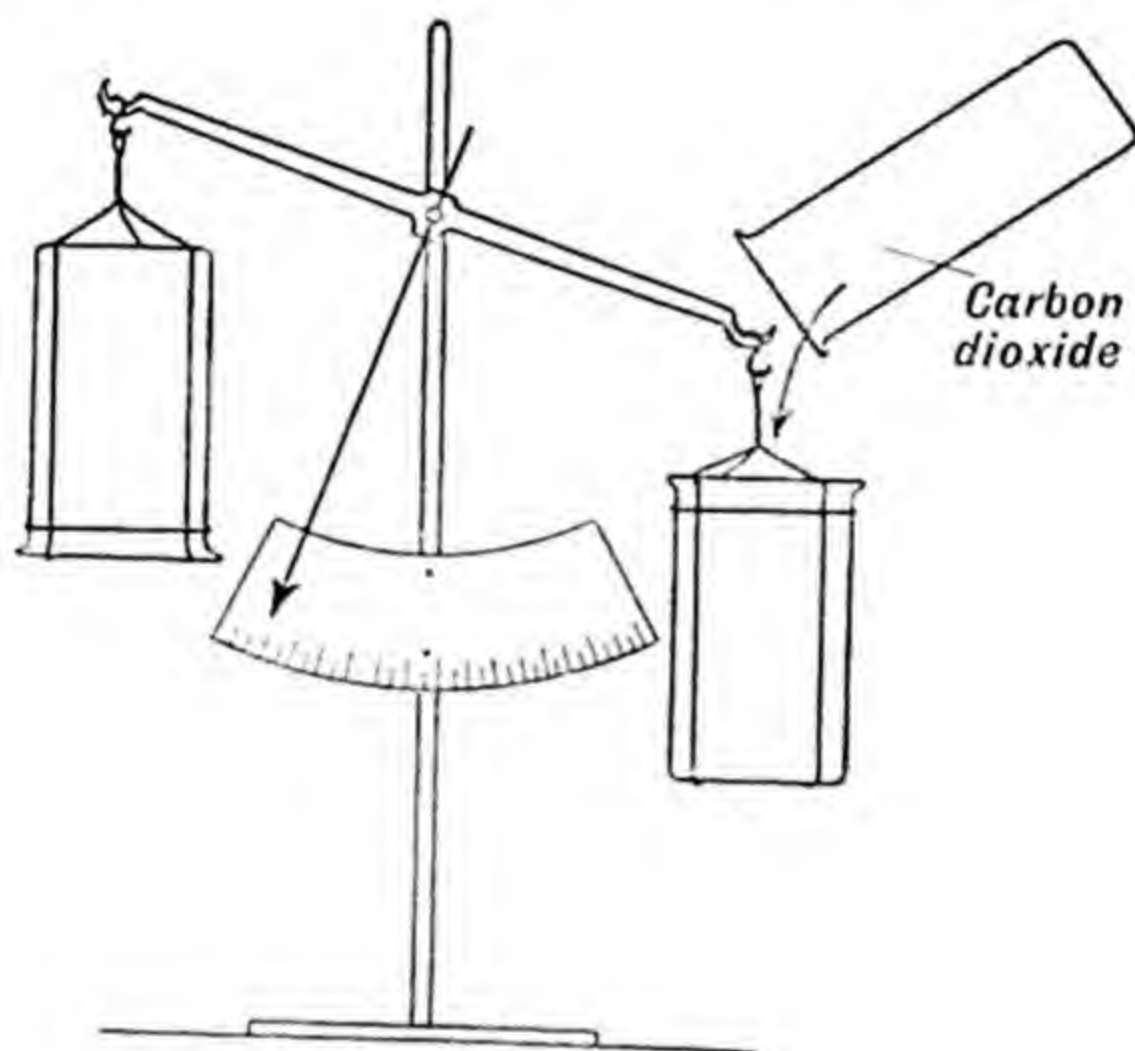


FIG. 79.

DEMONSTRATION THAT CARBON DIOXIDE IS HEAVIER THAN AIR.

(4) If a jar of carbon dioxide is held over a counterpoised beaker on a sensitive balance, and slowly inverted so as to pour the gas into the beaker (Fig. 79), the latter sinks, showing that carbon dioxide has passed into the beaker and is heavier than air. A taper inserted into the beaker is extinguished.

(5) If a jar of hydrogen is opened, mouth downwards, and slowly inclined so as to pour the gas upwards into an inverted counterpoised beaker, the latter rises, showing that hydrogen is lighter than air (Fig. 80).

These experiments show that different gases exist and that they may be recognised by their properties. This, in its time, was a most important advance in chemistry, and we owe it chiefly to the brilliant and ingenious work of Priestley.



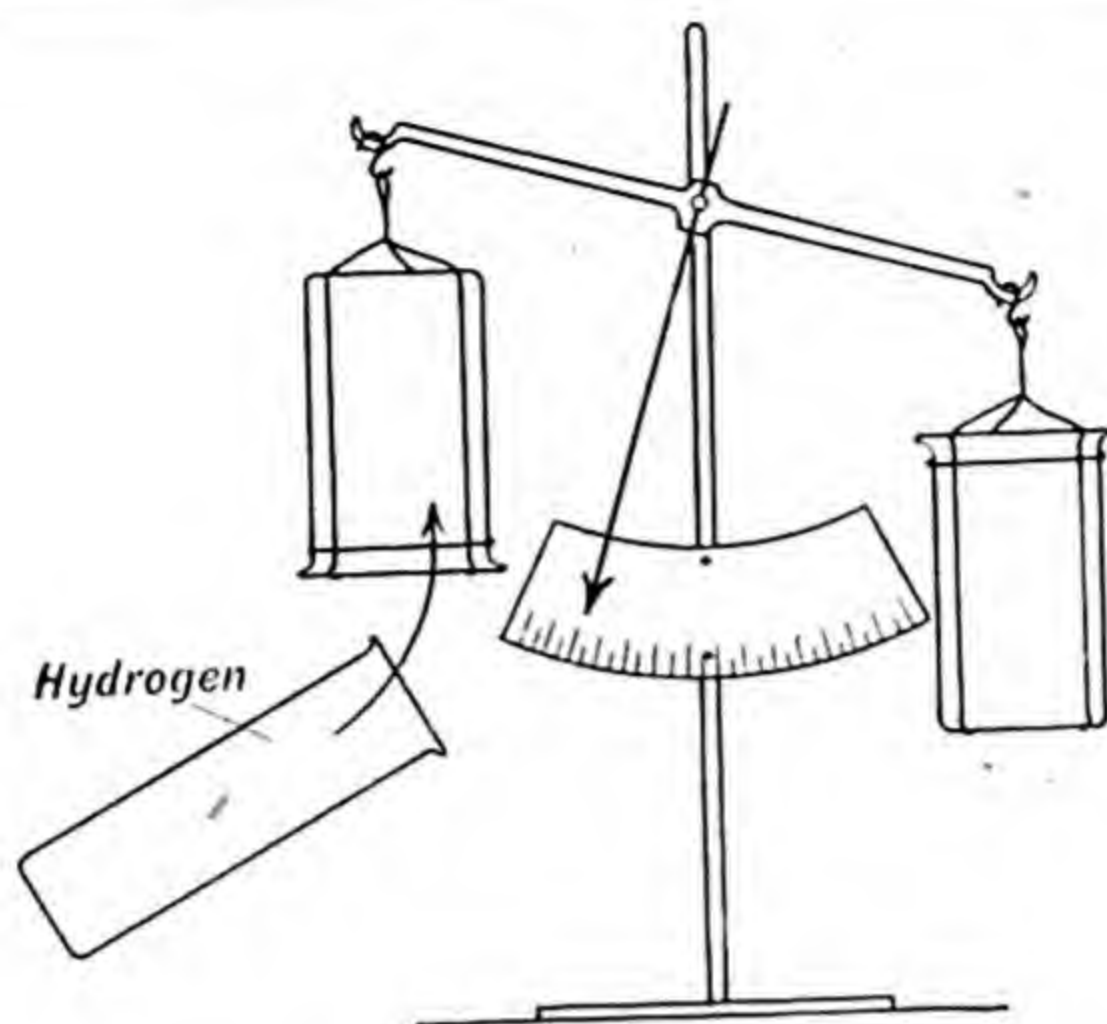


FIG. 80.

DEMONSTRATION THAT HYDROGEN IS LIGHTER THAN AIR.

**Combustion and the calcination of metals.**—There are two kinds of chemical change which, since they were investigated side by side, and depend on the same cause, may conveniently be described together. These are combustion, and the calcination of metals.

The alchemists attached great importance to the effects of heat on substances, and their writings describe many types of **furnaces**, and experiments made with them (Fig. 81). The metals, except gold and silver, were found to change when heated in open crucibles, and to leave a dross, which was called a **calx** (Latin *calx*, lime). It was noticed in the sixteenth century that this calx is heavier than the metal: the explanation usually given was that fire, or **caloric**, possessed weight, and was absorbed by the metal in forming the calx. A French physician, Jean Rey (1630), 'devoted several hours to the question,' without making many experiments, and

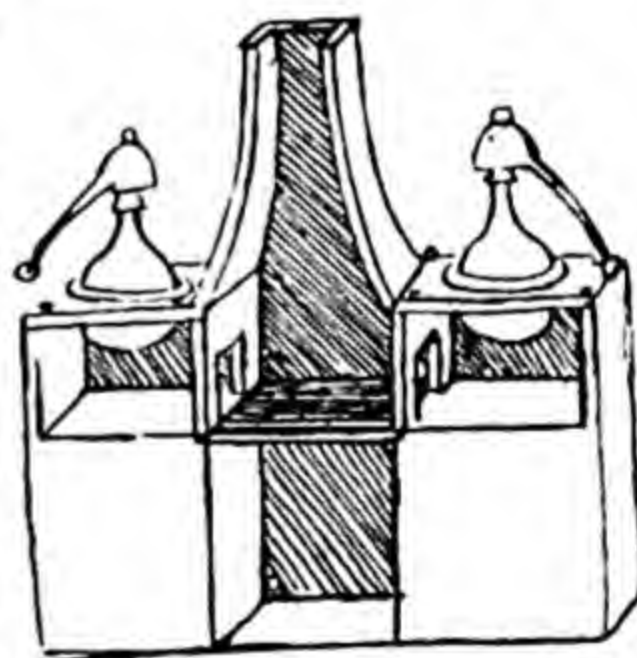


FIG. 81.—DRAWING OF A CHEMIST'S FURNACE, WITH TWO ALEMBICS (cf. Fig. 65), MADE BY THE FAMOUS ARTIST, LEONARDO DA VINCI (1452-1519). (From the *Codice Atlantico*, Milan.)

concluded that the air becomes thickened or adhesive by the action of the fire, and sticks to the calx. His ideas are very crude and inaccurate.

**Nitre air.**—Robert Boyle (1673) heated tin in a glass retort, and when it was melted, sealed off the neck and continued the heating for two hours. 'The retort was cooled, and the sealed tip of the neck broken. Air rushed in, 'because when the retort was sealed, the air within it was highly rarefied.' Boyle, from his method of experimenting, therefore did not notice, as Lavoisier did a century later, that some of the air was absorbed, although he found that the tin had increased in weight.

Boyle then showed that when sulphur was sprinkled on a red-hot plate under an exhausted air-pump receiver, it smoked but did not burn. On admitting air, 'divers little flashes were seen.' But if gunpowder were sprinkled on the hot plate under the vacuum receiver, he saw 'a pretty broad blue flame, like that of brimstone, which lasted so long as we could not but wonder at it.' Gunpowder could also burn under water. Boyle, therefore, somewhat reluctantly, concluded that *a flame can exist without air*, and that the increase in weight of metals on calcination is due to their absorption of 'igneous corpuscles,' which he considered to be material, and capable of being weighed in a balance. He observed that if charcoal is strongly heated in a closed retort it does not burn, but the *caput mortuum* (a fanciful name due to the alchemists, who represented a residue by the symbol of the skull and crossbones) becomes black again on cooling. If, however, air is admitted, the charcoal burns, and crumbles down to white ashes.

The latter experiment was repeated by Robert Hooke (at one time an assistant to Boyle), who, in his *Micrographia* (1665), put forward the first rational theory of combustion. Hooke found that a bit of charcoal or sulphur burns brilliantly when thrown into fused nitre.

If small quantities of nitre are fused in two hard glass test-tubes, or porcelain crucibles, and small fragments of charcoal and sulphur thrown into them, it will be found that the charcoal burns brightly and the sulphur burns with a beautiful blue flame.

On the basis of experiments Hooke concluded that :

"(1) Air is the universal dissolvent of all sulphurous [*i.e.*, combustible] bodies. (2) This action of dissolution produces a very great heat, and that which we call *fire*. (3) This dissolution is made by a substance inherent and mixed with the air that is



like, if not the very same with, that which is fixed in saltpetre [nitre]." In this way he was able to explain the combustion of gunpowder, one constituent of which is nitre, in the absence of air.



FIG. 82.—JOHN MAYOW. 1641-1679.

John Mayow, in a book entitled *Tractatus quinque medico-physici*, published at Oxford in 1674, elaborated a theory similar to that of Hooke, supported by descriptions of experiments. He concluded that air consists of two gases; one is the nitre-air of Hooke, called by Mayow *spiritus nitro-aereus*, or the *nitro-aerial spirit*, which is concerned in combustion and respiration; and the other is an air incapable of supporting either combustion or respiration.

(1) Mayow inverted a large glass globe over a lighted candle standing in water, equalising the levels of the latter by means of a siphon, which was then quickly withdrawn. The water rose inside the globe, showing that some air had disappeared. When

the candle was extinguished, a large bulk of air was left, but this would not support the combustion of sulphur or camphor lying on a small shelf inside the globe, when they were heated by a burning glass (Fig. 83).

The contraction of air in a globe standing over water when a candle was burnt in it had been described by Philo of Byzantium about the first century A.D., if not earlier.

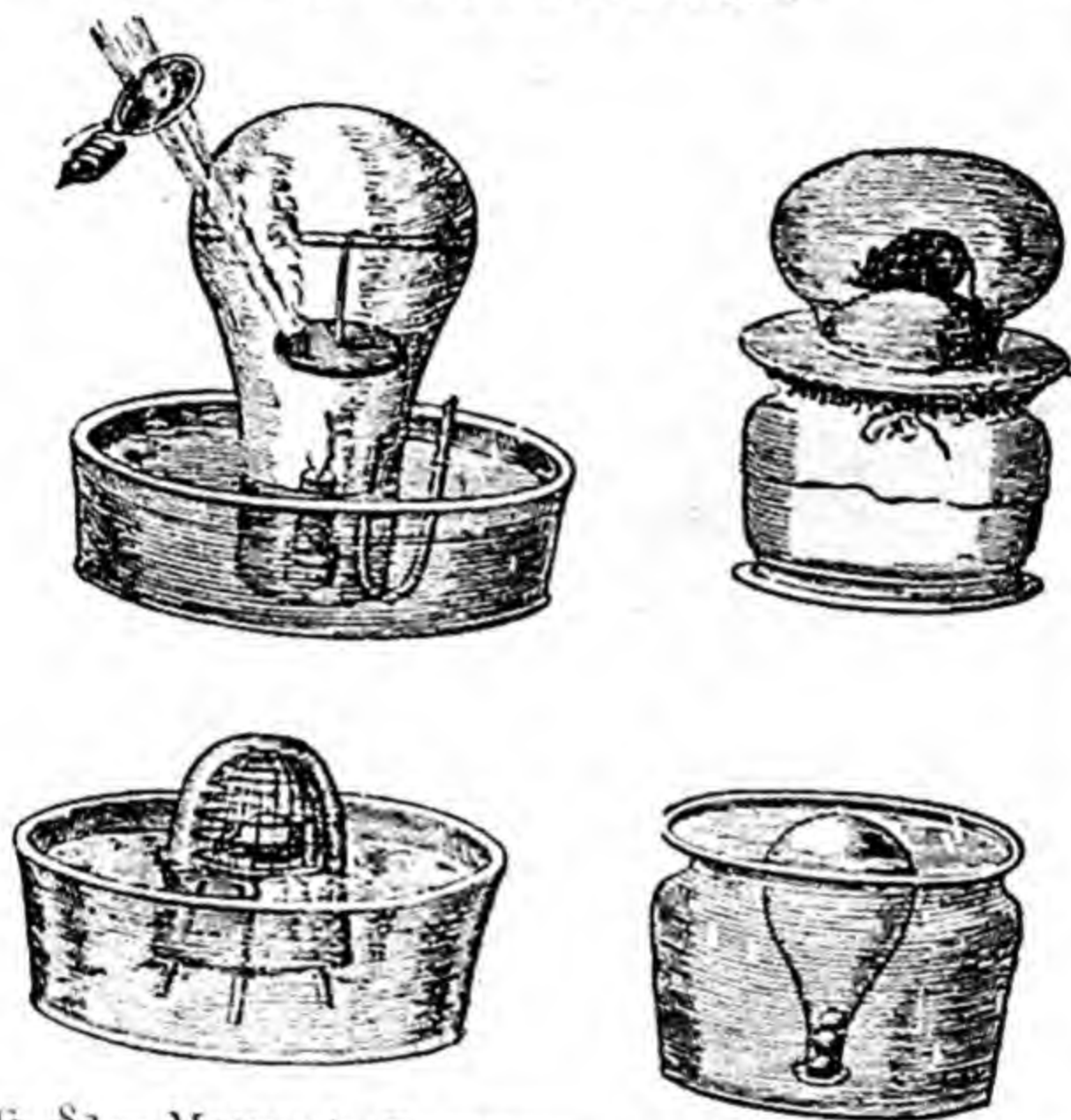


FIG. 83.—MAYOW'S EXPERIMENTS (from his *Tractatus quatuor medico-physici*, 1674).

THE ILLUSTRATIONS DEPICT THE EXPERIMENTS ON COMBUSTION AND ON THE RESPIRATION OF A MOUSE DESCRIBED IN THE TEXT; ALSO THE CONTRACTION OF AIR CONFINED OVER WATER BY THE RESPIRATION OF A MOUSE, AND THE COLLECTION OF 'AIR' (NITRIC OXIDE) FROM IRON BALLS AND DILUTE NITRIC ACID IN AN INVERTED FLASK.

(2) Mayow found that air in which a mouse had died would not support combustion, and a mouse in a vessel with a burning lamp lived only half as long as it did without the lamp. When a mouse was kept in a vessel of air closed by a bladder (Fig. 83), the contraction of the air was perceptible by the bulging inwards of the membrane owing to the pressure outside.

(3) Gunpowder rammed into a paper tube and ignited continued to burn under water. The air fixed in nitre can therefore



take the place of ordinary air in supporting combustion, and since things burn more brilliantly in fused nitre than in common air, the nitre must contain an abundant supply of nitre air, which is the part of common air concerned in combustion.

(4) Mayow refers to an experiment of calcining metallic antimony on a marble slab by means of a burning-glass. Although



FIG. 84.—G. E. STAHL, 1660-1734.

abundant fumes were evolved, the calx weighed more than the metal. The calx was found to be identical with that formed by the action of nitric acid on the metal.

Neither Hooke nor Mayow isolated nitre air; this can be done by heating nitre strongly in a hard glass test-tube, when it gives off bubbles of nitre air. A glowing chip introduced into this bursts into flame. The beginnings of a true theory of combustion

which resulted from the work of Boyle, Hooke and Mayow was overshadowed by the theory of phlogiston.

**Theory of phlogiston.**—John Joachim Becher, who was born at Speyer in 1635 and was for a time in England, where he died in 1682, published in 1669 a book called *Physicæ subterraneæ*, in which he stated that the constituents of bodies are air, water, and three earths, one of which is *inflammable* (*terra pinguis*); the second *mercurial*; the third fusible, or *vitreous*. These correspond with the sulphur, mercury, and salt of the alchemists. On combustion, the 'fatty earth' burns away.

In 1703 Becher's treatise was republished by George Ernst Stahl, professor at Halle, a good chemist and an excellent teacher, who, in his lectures and text-book (*Fundamenta Chymiae*, 1723), popularised Becher's views in an improved form. He gave the name **phlogiston** (from the Greek, *phlox* = flame; a flame-coloured flower is called a *phlox*) to the *terra pinguis* of Becher. When bodies burn, or are calcined, phlogiston escapes with a rapid whirling motion; when the original bodies are recovered by reduction, phlogiston must be replaced. Oil, wax, charcoal, and sulphur, which are all combustible bodies, are rich in phlogiston, and may be used to restore it to a burnt material from which it has escaped. Zinc on heating to redness burns with a brilliant flame, hence phlogiston ( $\phi$ ) escapes. The white residue is called calx of zinc. If it is strongly heated with charcoal (rich in phlogiston) zinc distils off. Hence: **calx of zinc +  $\phi$  = zinc**. Similarly with other metals. If phosphorus is burnt, it produces an acid matter, and much heat and light are evolved. Hence: **phosphorus = acid +  $\phi$** . If the acid is heated with charcoal, phlogiston is absorbed and phosphorus is reproduced.

Stahl's theory had one advantage in that it united a great many previously isolated facts, and it became almost universally accepted during the eighteenth century, although Boerhaave in his important text-book (*Elementa Chemiae*, 1732) does not mention it.

During this period the increase in weight of metals on calcination was usually ignored as of little importance, or as belonging to physics rather than to chemistry, although the fact was destined later to overturn the whole theory of phlogiston.

This increase of weight is readily shown by an experiment. Some finely divided *reduced iron* is taken up by a horse-shoe magnet, counterpoised from one arm of a sensitive balance (Fig. 85), a piece of asbestos paper being placed in the pan



underneath the magnet. If a spirit-lamp flame is applied to the tufts of iron adhering to the magnet, the powder begins to glow, and after calcination falls from the magnet. The pan on

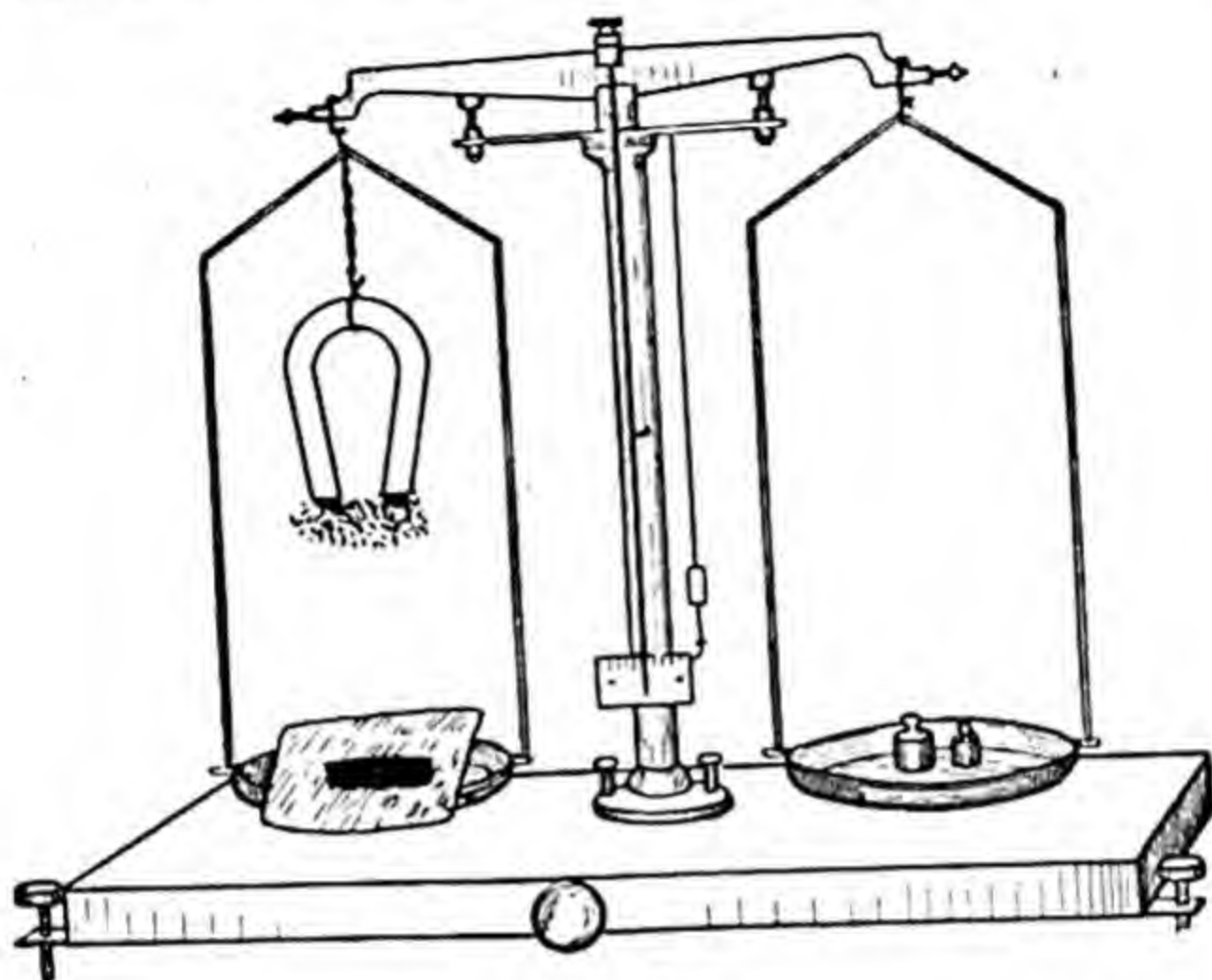


FIG. 85.

INCREASE IN WEIGHT OF FINELY DIVIDED IRON ON BURNING IN AIR.

the side of the balance where the magnet is suspended sinks, showing that the iron increases in weight during calcination. The iron calx left is found to be black in colour, whereas the original iron powder is grey.

**Scheele's experiments on fire and air.**—Carl Wilhelm Scheele (1742-1786) was a firm believer in Stahl's theory. A poor apothecary of Sweden, he made a great number of chemical discoveries of the very first rank, those on combustion being published in his treatise *On Air and Fire*. These experiments were made chiefly before the autumn of 1770, and all prior to 1773, but the book did not appear until 1777, when many of Scheele's discoveries had been made independently, and published, by Priestley in England. Scheele's priority was only established in 1892, from his original laboratory notes.

In his first set of experiments Scheele noticed the contraction of a confined volume of air standing in contact with various materials. He used, for example, a solution of liver of sulphur (*hepar sulphuris*), a solution of sulphur in lime-water, linseed oil, and iron filings moistened with water, all of which, he observes,

are rich in phlogiston, or, as he called it, the **inflammable substance**. In all cases there was a *loss of air*.

This contraction is easily shown by exposing moist liver of sulphur, moist iron filings, and a piece of phosphorus stuck on a wire, to air in three glass tubes divided into five parts and



FIG. 86. CARL WILHELM SCHEELE, 1742-1786.

standing over water (Fig. 87). After a few days one-fifth of the air will have been absorbed and the residual gas will extinguish a taper.

The inflammable substance was not contained in the residual gas, which differed from common air. For, if this gas had been formed by the union of common air with phlogiston, and contraction, it should be denser than common air. But: 'a very thin flask which was filled with this air, and most accurately



weighed, not only did not counterpoise an equal volume of ordinary air, but was even somewhat lighter." Thus, "the *air is composed of two fluids*, differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, whilst the other, which composes between the third and fourth part of the whole mass of the air, is peculiarly disposed to such attraction." These two constituents of common air Scheele called **Foul Air** and **Fire Air**: they were afterwards named nitrogen and oxygen, respectively.



FIG. 87.—ABSORPTION OF PART OF THE AIR BY PHOSPHORUS.

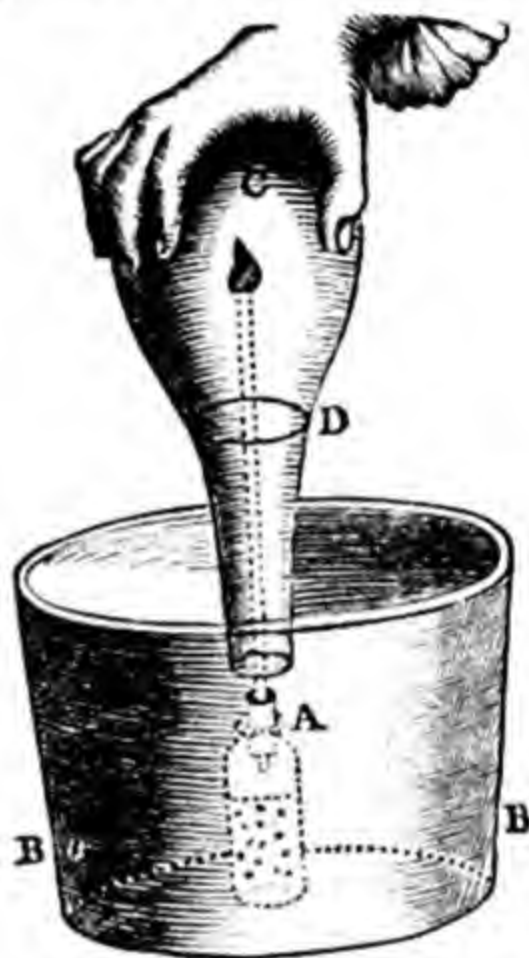


FIG. 88.—COMBUSTION OF HYDROGEN IN AIR: SCHEELE'S EXPERIMENT.

THE HYDROGEN WAS GENERATED IN THE BOTTLE A, IMMERSED IN A TUB OF HOT WATER B, AND THE HYDROGEN FLAME C, BURNT INSIDE THE INVERTED FLASK D. THE WATER ROSE IN THE FLASK.

Scheele next placed a little phosphorus in a thin flask, corked the latter, and warmed it until the phosphorus took fire. A white cloud was produced, which attached itself to the sides of the flask in white flowers of 'dry acid of phosphorus.' On opening the flask under water, the latter rushed in, and occupied a little less than one-fifth of the flask. By allowing phosphorus to stand for six weeks in air in the same flask, until it no longer glowed, again some of the air was lost.

Scheele then burnt a hydrogen flame under a glass globe standing over water (Fig. 88). The water at once began to rise, until it filled one-fourth of the flask, when the flame went out.

Scheele assumed that the inflammable substance (hydrogen) had combined with the fire air, and since he was unable to find the product of the combination (he missed the dew deposited on the flask) he assumed that it was *heat*. He therefore tried to decompose heat and set free the fire air by several methods: heating nitre either alone or with sulphuric acid, heating mercury oxide, etc. In this way he made an immense step forward, because he was able to obtain pure fire air, which he found was a colourless gas in which a taper burned with great brilliancy.

He found that it is *completely* absorbed by moist liver of sulphur. When he burnt phosphorus in a thin flask of it, the flask burst on cooling. With a thicker flask, the cork could not be taken out under water, but could be pushed in, when water rushed in and filled the flask. A hydrogen flame continued burning in the gas until seven-eighths were absorbed.

When fire air was added to the foul air left after combustion of hydrogen, etc., in air, so as to restore the original volume, the mixture had all the properties of ordinary air, *e.g.*, it left the same residue after standing over liver of sulphur.

If four-fifths of a gas-jar, divided into 5 parts, are filled with nitrogen ('foul air') and then the remaining fifth is filled with oxygen ('fire air') a taper burns in the mixture exactly as it does in common air, although the taper is extinguished in the nitrogen alone and burns with great brilliance in oxygen.

Scheele placed various animals and insects in confined volumes of air, taking care to put along with them their appropriate foods. He found that they ultimately died; *aerial acid* (Black's *fixed air*, p. 414) was produced, and a contraction of the air resulted, the residue extinguishing a flame. Similar results were found with sprouting peas. Two large bees were placed in a bottle of fire air over milk of lime, Scheele having 'provided some honey for their stay.' After eight days the bottle was almost completely filled with liquid, and the bees were dead. He also noticed that the fire air is partly dissolved out of common air when this stands over water which had been boiled. A candle burns more brightly in the air expelled from the water by boiling than in common air.

**Priestley's experiments on dephlogisticated air.**—Whilst Scheele was carrying out his experiments in Sweden, Priestley in England was also busy with experiments on gases. He came into the possession of a good convex lens or *burning glass* and by its aid tried to extract 'air' from various chemicals



given to him by his friend Warltire. Among these was red precipitate, or *mercurius calcinatus per se*, obtained by heating mercury in air, the nature of which had long been a puzzle to chemists. The substances were heated by focusing the sun's rays on them in small phials filled with, and inverted over, mercury.

'Having procured a lens of twelve inches diameter, and twenty inches focal distance [the statue of Priestley at Leeds represents him performing this famous experiment (Fig. 89)], I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious [*i.e.*, artificially prepared] would yield. . . . With this apparatus, after a variety of other experiments, . . . on the 1st August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame. . . . I was utterly at a loss how to account for it.'

Priestley found that a mouse lived twice as long in the new air as in the same confined volume of common air, and revived afterwards when taken out. He breathed it himself, and fancied his 'breast felt peculiarly light and easy for some time afterwards'—hence he recommended its use in medicine (it is now used in the treatment of gas poisoning and pneumonia). 'Who can tell,' he says, 'but that, in time this pure air may



FIG. 89.—STATUE OF PRIESTLEY AT LEEDS.

become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it.'

Priestley assumed, from the teachings of Stahl, that a candle on burning gives out phlogiston, and is extinguished in a closed vessel after a time because the air becomes saturated with phlogiston. Ordinary air, therefore, supports combustion because it is only partially saturated with phlogiston, and can absorb more of it. Substances burn in air with only a moderate flame, whereas in the new air the flame is vivid; Priestley, therefore, concluded that the new gas must contain little or no phlogiston, and hence he called it *dephlogisticated air*. The gas left when bodies burnt out in ordinary air was named, for a similar reason, *phlogisticated air*:

*Phlogisticated Air* [Nitrogen] = *Air* +  $\phi$ . (Scheele's Foul Air.)

*Dephlogisticated Air* [Oxygen] = *Air* -  $\phi$ . (Scheele's Fire Air.)

**Lavoisier and the antiphlogistic theory.**—Antoine Laurent Lavoisier (1743-1794), the famous French scientist, began his experiments on combustion in 1772. He found that metals when calcined increase in weight, as pointed out by Rey in 1630, and an equal weight of air is absorbed. In a given volume of air, calcination proceeds only to a fixed limit, and an unabsorbed gas remains. Phosphorus burns in a confined volume of air; in this diminished volume a taper is extinguished, and the white powder formed weighs more than the phosphorus.

He concluded that these *substances on burning take something from the air*.

Lavoisier next modified Boyle's experiment of calcining tin and lead, by using weighed *sealed* retorts. He found no change in weight, which disproved Boyle's theory, until air was allowed to enter. On heating the *calx of lead* with charcoal he found it lost in weight, and 'an air was abundantly evolved.' Thus something is taken from the calx in forming the metal, and this must be 'an air.' Further Lavoisier did not go.

But in October, 1774, Priestley visited Paris with Lord Shelburne, and told Lavoisier at dinner of his discovery of dephlogisticated air, saying he 'had gotten it from *precip. per se* and also *red lead*'; whereupon, he says, 'all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise.'

Priestley's statement is noteworthy, and it seems that up to this time Lavoisier ~~had not suspected~~ that it is only a *part* of the air which is concerned in combustion and respiration, although,



as we have seen, Scheele knew this some years before. Lavoisier, however, was quick to see the important bearing of Priestley's discovery on his own unfinished work; he was able to prove that it is dephlogisticated air which is absorbed in the calcination



FIG. 90.—ANTOINE LAURENT LAVOISIER, 1743-1794

of metals, by a famous experiment, described in his *Traité de Chimie*, 1789.

He heated 4 oz. of mercury in a retort which communicated with a measured volume of air in a bell-jar over mercury. The volume of air in the bell and in the retort was 50 cu. in. After a time he noticed the formation of red specks and scales of calx on the surface of the mercury. After twelve days the scales no longer increased; the fire was removed, and the experiment

stopped. The air had contracted to 42 cu. in., and the gas left was 'mephitic air,'\* which Lavoisier at first called *atmospheric mofette*. He afterwards named it *azote*, and Chaptal called it *nitrogen* in 1790. The scales, or mercury calx (*mercurius calcinatus per se*), were collected and found to weigh 45 grains. They were transferred to a small retort and heated; 8 cu. in. of dephlogisticated air, which was 'an elastic fluid, much more capable of supporting respiration and combustion than ordinary air,' and hence called by Lavoisier *vital air*, or *air eminently respirable*, were obtained, together with  $41\frac{1}{2}$  grains of mercury.

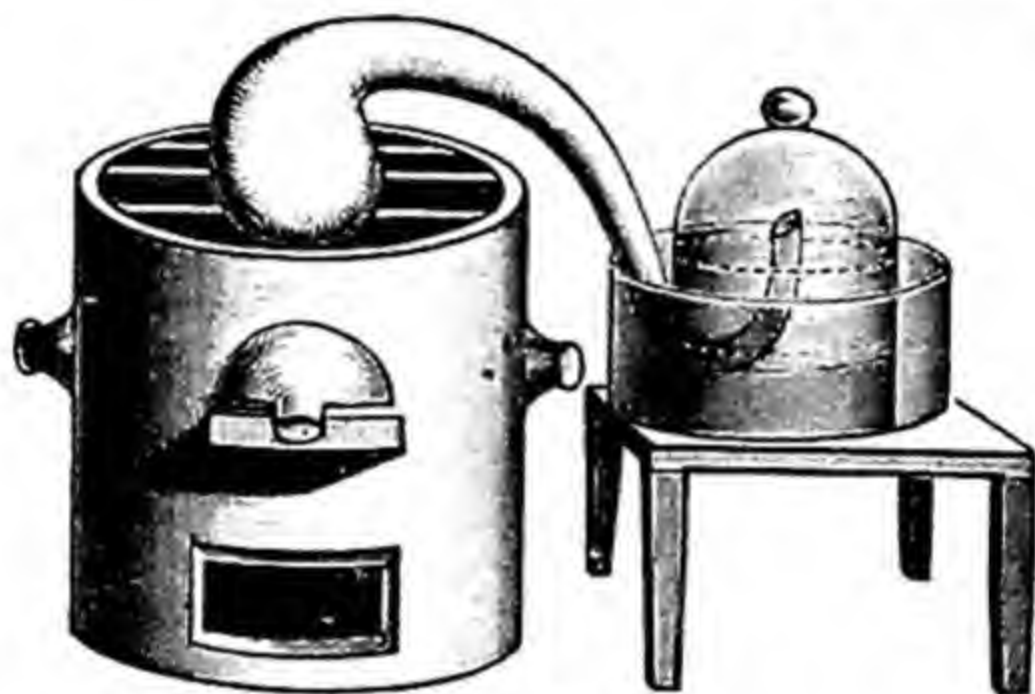


FIG. 91.

LAVOISIER'S APPARATUS FOR HEATING MERCURY IN A CONFINED VOLUME OF AIR.

When this vital air was added to the atmospheric mofette, ordinary air was formed without any evolution of heat or light, hence air is probably simply a mixture of these two gases (as had previously been suggested by Scheele).

The apparatus used by Lavoisier in this experiment is shown in Fig. 91, which is reproduced from Lavoisier's *Traité de Chimie*, all the illustrations in that book being drawn by Madame Lavoisier.

Lavoisier made experiments on the combustion of substances in vital or 'pure' air, and summed up his conclusions in the four statements:

- (1) Substances burn only in pure air (*i.e.* oxygen).

\* *Mephitis*, a noxious exhalation, Vergil, *Aeneid*, vii, 84: the name 'mephitic air' was used both for nitrogen and carbon dioxide (see p. 372).



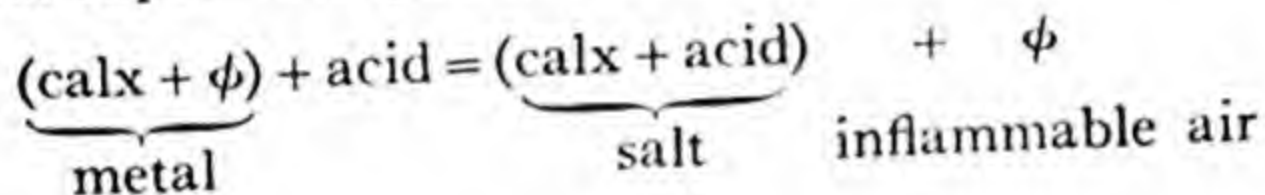
(2) Non-metals, such as sulphur, phosphorus, and carbon, produce acids on combustion; hence the gas was called oxygen ( $\acute{o}\xi\eta\varsigma = acid$ ).

(3) Metals produce bases on absorption of oxygen.

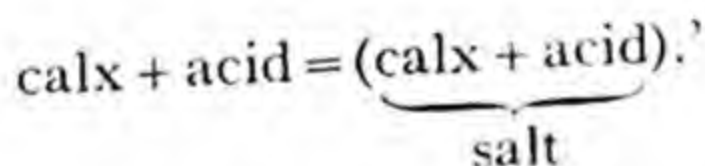
(4) Combustion is in no case due to an escape of phlogiston, but to chemical combination of the combustible substance with oxygen.

These statements comprise the fundamental tenets of the antiphlogistic theory.

Lavoisier's conclusions were not accepted at once; Black in Scotland, and a few French chemists, supported them, but there was one great difficulty still to be overcome. A metal like tin or zinc dissolves in an acid giving inflammable air, and a salt is left on evaporating the solution, which, on strong heating, parts with its acid and leaves the calx of the metal. The same salt is formed when the calx is dissolved in the acid, but no inflammable air is then evolved. Whence comes the inflammable air in the first experiment? This was an easy question for the phlogistonists. 'Inflammable air,' said they, 'is phlogiston; the metal is (calx + phlogiston); and the salt is (calx + acid). In the first experiment you have, clearly:



in the second:



This difficulty was serious: Lavoisier was unable to offer an explanation. The key was first supplied by the researches of Cavendish on the formation of water from inflammable air and dephlogisticated air. In the meantime the French Revolution had broken out. On the 19th Floreal of the Year II (8th May, 1794) Lavoisier was condemned by the ferocious Coffinhal, Vice-President of the Tribunal, on the charge of having put water into the soldiers' tobacco. A plea entered on his behalf, on the ground of his great scientific services, was vain. 'The Republic has no need of men of science: justice must take its course,' was Coffinhal's reply. The guillotine fell and France lost her most illustrious man of science. The science of chemistry as we know it really began with Lavoisier.

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SUMMARY OF EARLY WORK ON COMBUSTION AND ON THE COMPOSITION OF THE ATMOSPHERE.

1660. Boyle found by experiment that only part of the air is absorbed in combustion and respiration.
1665. Robert Hooke suggested that the part of the air absorbed in combustion and respiration is also contained in saltpetre (nitre) and called it **nitre air**.
1674. John Mayow carried out many experiments on combustion and respiration and confirmed Hooke's suggestion so far as he was able, without isolating nitre air (which he called the **nitro-aerial spirit**).
- 1669-1702. Becher and Stahl put forward the theory of **phlogiston**, an imaginary constituent of combustible bodies which escapes from them when they burn.
1727. Hales described in his *Vegetable Staticks* the production of various gases but did not distinguish them from common air.
1766. Cavendish described the preparation and properties of two gases, hydrogen (inflammable air) and carbon dioxide (fixed air).
1774. Priestley, after investigating other gases and showing how soluble gases could be collected over mercury, made the discovery of oxygen, which was Hooke's nitre air. Priestley called it **dephlogisticated air**.
- 1770-73. Scheele independently discovered oxygen, which he called **fire air** and showed that it is mixed in the atmosphere with another gas which he called **foul air**. Only fire air is absorbed in combustion and respiration.
- 1774-5. Lavoisier recognised that fire air (or dephlogisticated air) is an element, which he called **oxygen**. He proved by experiments that combustion is not the escape of phlogiston from a body but the absorption of oxygen. The other constituent of the air he called **azote**, but it was afterwards called **nitrogen** by Chaptal.



## CHAPTER VI

### THE COMPOSITION OF WATER

**The work of Cavendish.**—We have seen how one of the 'four elements' of antiquity, viz. *air*, was shown to be a mixture



FIG. 92.—HENRY CAVENDISH, 1731-1810.

of two elements, oxygen and nitrogen, about the end of the eighteenth century. The turn of water came next; this proved

to be a compound, not a mixture, of two gases, oxygen and hydrogen.

Priestley in 1781 observed that when a mixture of *dephlogisticated air* (oxygen) and *inflammable air* (hydrogen) is ignited, it explodes violently. Warltire noticed that the sides of the bottle, after the explosion, are bedewed with moisture.



FIG. 93.—CAVENDISH'S FIRING GLOBE ('EUDIOMETER').

(From a Photograph of what is believed to be the original apparatus in the University of Manchester.)

By firing the gases in a closed copper globe with the electric spark, Priestley thought he found that there was a slight loss of weight, which he put down to the escape of heat.

Cavendish in 1781 ignited a mixture of common air and inflammable air in a glass globe by means of the spark. He found that, with 423 vols. of inflammable air to 1000 vols. of common air, 'almost all the inflammable air and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass.' There was no change in weight after explosion. He found the ratio of the combining volumes of hydrogen and oxygen to be 202 : 100.

To examine the nature of the dew, Cavendish performed an experiment similar to the following.

A jet of hydrogen is burnt under a glass flask filled with cold water. Moisture at once condenses on the outside of the flask, and the drops may be received in a beaker placed under the flask. The liquid collected is easily recognised as water.

Cavendish now prepared a mixture of dephlogisticated air and inflammable air in a bell-jar over water. The end of a siphon tube, attached to the previously exhausted glass firing-globe or eudiometer (Fig. 93), was covered with a bit of wax and passed inside the jar. The wax was knocked off, and on opening the stopcock the globe was filled with the mixture. The cock



was closed, and the mixture fired by a spark. The gas 'lost its elasticity,' and on opening the stopcock the globe was again

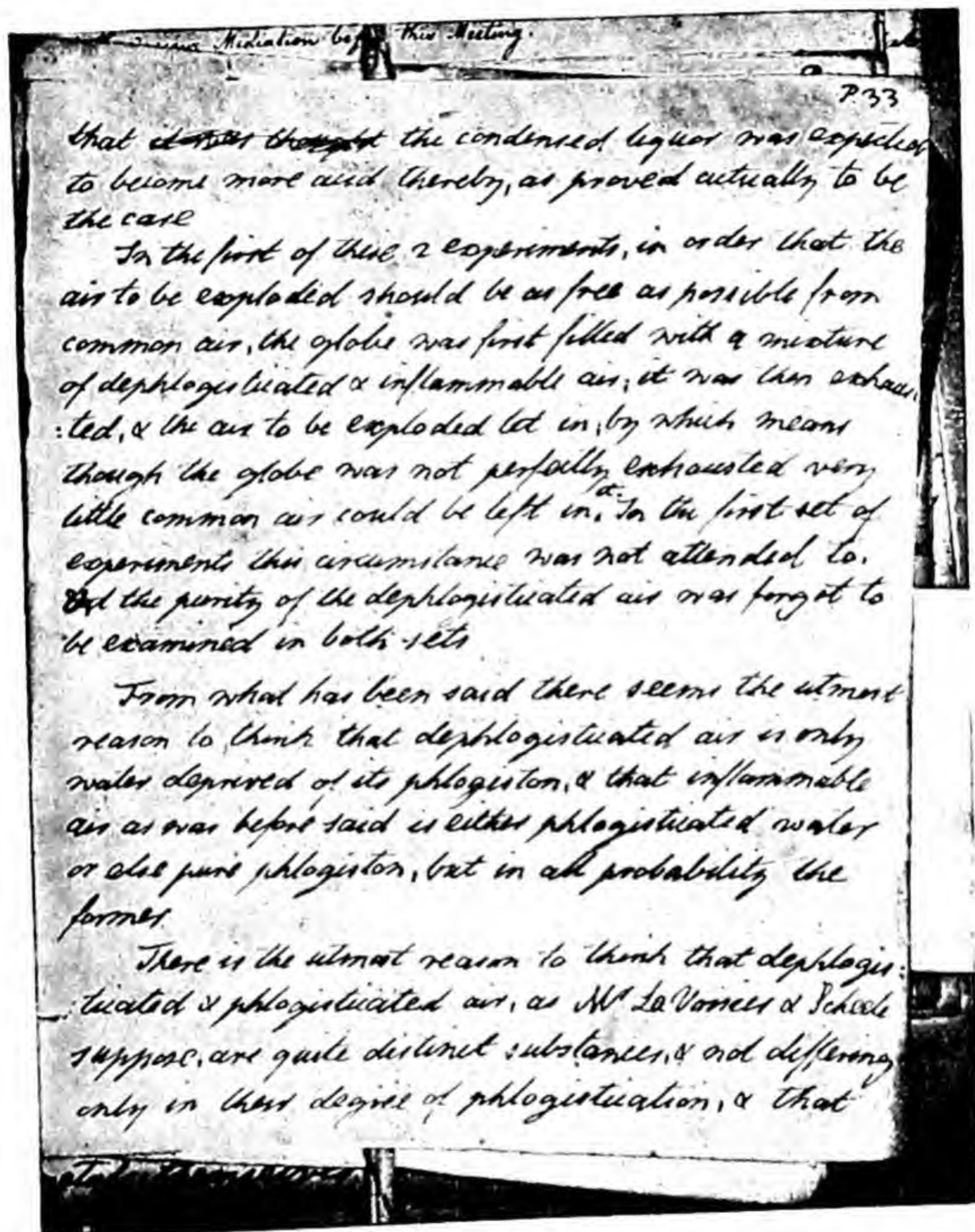


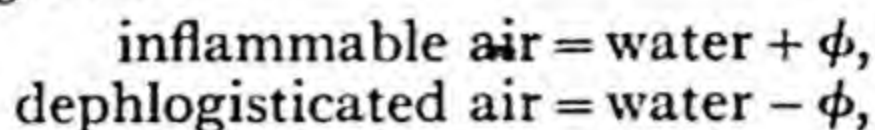
FIG. 94.

PART OF THE MS. OF CAVENDISH'S MEMOIR, IN THE ARCHIVES OF THE ROYAL SOCIETY.

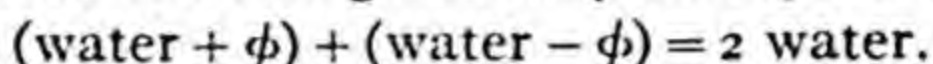
filled with the gas, which took the place of that converted into liquid water by the explosion. Cavendish delayed publication

of his memoir until 1784. His conclusions were curious: they are given in Fig. 94, in Cavendish's own handwriting.

Cavendish therefore thought that water *pre-existed in the two gases, and its formation on explosion was simply due to a transfer of phlogiston* :



hence the union of the two gases may be represented as :



Cavendish was too firmly attached to the phlogiston theory to accept the correct explanation, although he mentions the latter as an alternative in his memoir.

**Lavoisier's explanation of Cavendish's experiments.**—Lavoisier had been considerably puzzled by the product of the combustion

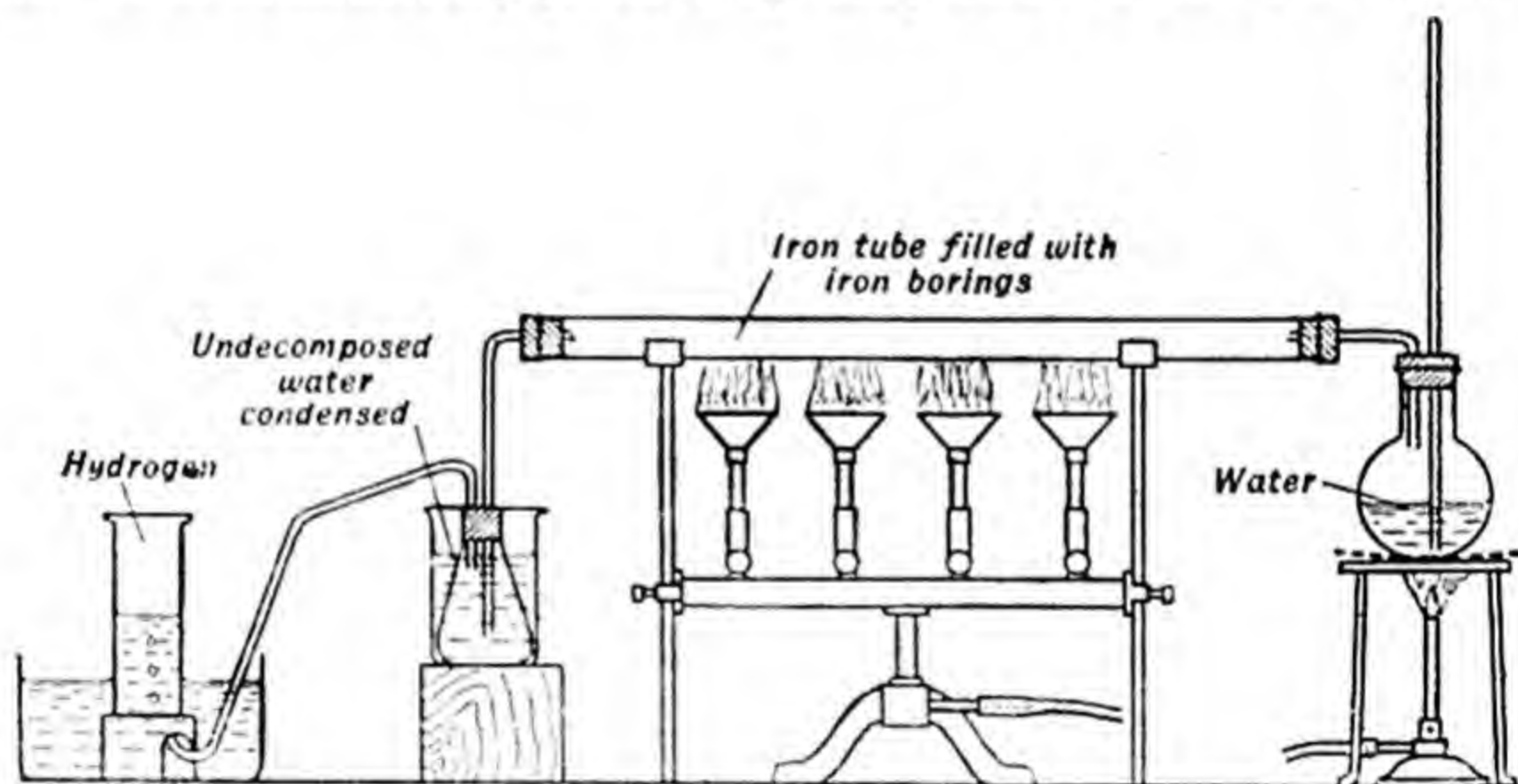


FIG. 95.

THE DECOMPOSITION OF STEAM BY PASSING IT OVER RED-HOT IRON. THE OXYGEN OF THE STEAM IS TAKEN BY THE IRON TO FORM OXIDE OF IRON AND THE HYDROGEN IS SET FREE AND MAY BE COLLECTED.

of hydrogen in oxygen, which he thought, on the basis of his theory (p. 103), must be an acid. In 1783 he resolved to make the experiment of burning hydrogen in oxygen on a larger scale, so that the product, whatever it was, should not escape his notice. In May or June of that year, however, Sir Charles Blagden, who was formerly Cavendish's assistant, visited Lavoisier, and told him of Cavendish's experiments. Lavoisier at once saw the importance of the result, and on June 24th, 1783, he repeated the experiments in the presence of Blagden. In 1784 he published



the work, and gave a clear statement of the composition of water. In 1788 Lavoisier said: 'Water is nothing but oxygenated hydrogen, or the immediate product of the combustion of oxygen gas with hydrogen gas, deprived of the light and caloric [heat] which disengage during the combustion.'

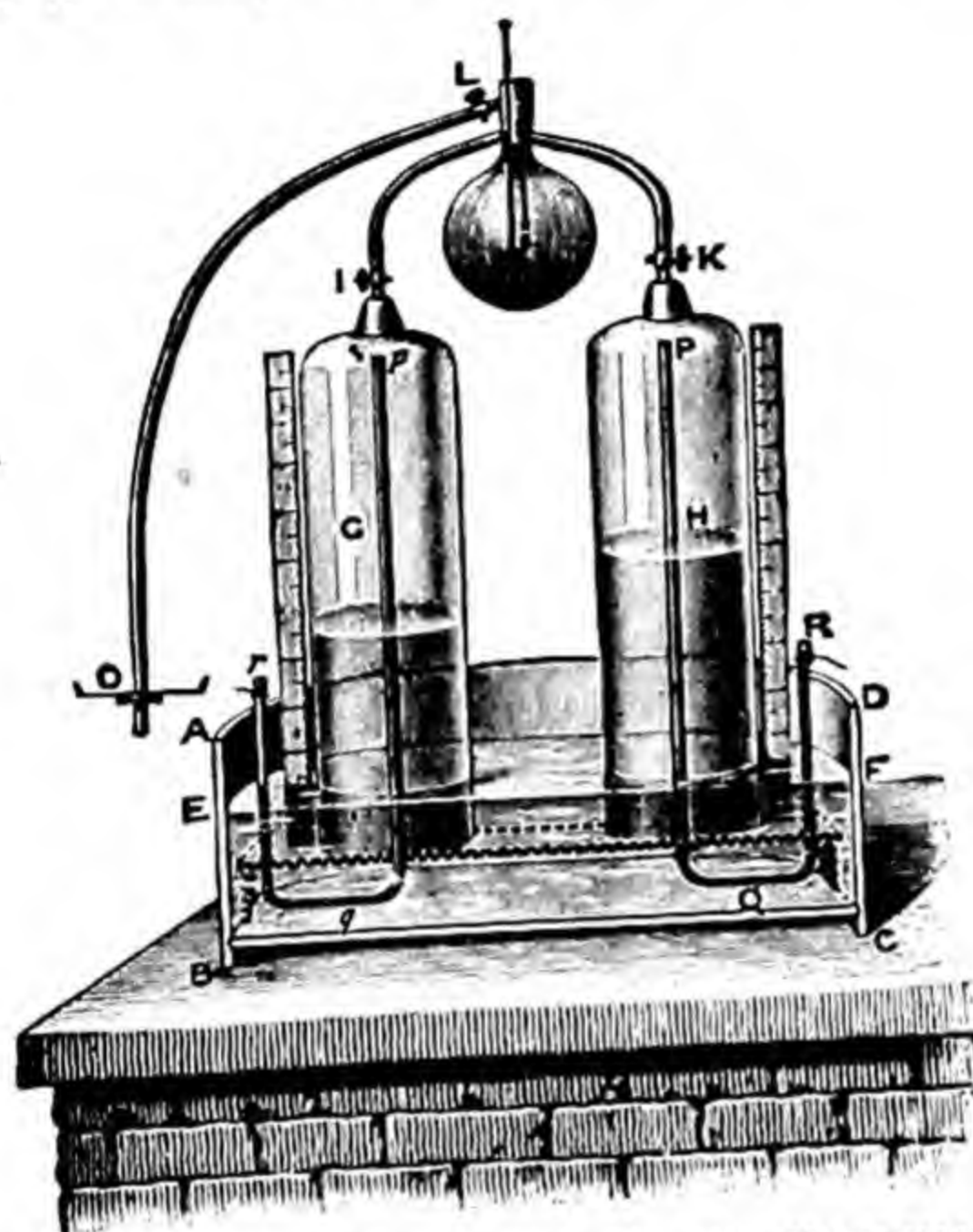


FIG. 96.—MONGE'S EXPERIMENT ON THE COMBINATION OF HYDROGEN AND OXYGEN GASES.

THE GASES WERE COLLECTED THROUGH SYPHON-TUBES, *pr*, *PR*, IN THE CYLINDERS G and H; THEY PASSED THROUGH THE STOPCOCKS, I and K, TO THE GLOBE, M, PREVIOUSLY EXHAUSTED THROUGH THE TAP, L, LEADING TO AN AIR-PUMP AT O. THE MIXED GAS WAS THEN EXPLODED BY AN ELECTRIC SPARK AT M, AND THE PROCESS REPEATED.

In 1784 Lavoisier and Meusnier decomposed water by passing its vapour over iron borings heated to redness in a gun-barrel. Hydrogen was liberated, and the iron converted into the same black oxide as is produced when iron burns in oxygen. The experiment may be carried out as follows.

A piece of *weldless* iron pipe is loosely packed with iron turnings, placed in a combustion furnace (Fig. 95), and connected with a flask of water at one end, and an empty flask and gas delivery tube at the other. The iron tube is heated to red-

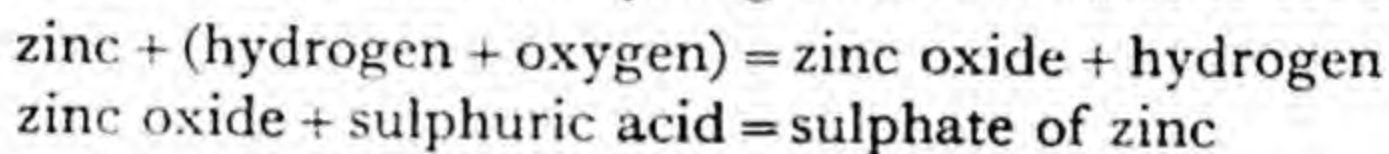
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ness and the water in the flask boiled. Water collects in the empty flask, showing that the decomposition is not complete, but bubbles of gas are evolved from the delivery tube which may be collected in the jar and shown to be hydrogen.

The decomposition of steam is more easily shown by inserting a piece of burning magnesium ribbon into a large conical flask in which a little water is boiling vigorously. The metal burns brightly in the steam, and the hydrogen produced burns at the mouth of the flask with a pale flame; white magnesium oxide is left after the combustion.

The French man of science, Monge, in 1783 exploded hydrogen and oxygen, drawn from two jars, in a previously evacuated glass globe, with firing wires (Fig. 96). No fewer than 372 successive explosions were made, producing four ounces of water, and the hydrogen and oxygen combined in the ratio of 1.95 : 1 by volume. The result is less accurate than that of Cavendish.

Lavoisier was now able to explain the difficulty mentioned on p. 103. A metal such as zinc, dissolving in dilute acid, takes oxygen from water to form oxide of zinc, which dissolves in the acid to form a salt, and the hydrogen of the water is set free :



Lavoisier regarded the acid as an oxide; at present it is regarded as (oxide + water), so that the hydrogen really comes from the acid.

From 1785 the theory of phlogiston gradually disappeared. At the beginning of the nineteenth century practically every chemist except Priestley (whose work has done so much to overturn it) had abandoned the theory.

**The electrolysis of water.**—In 1800 Nicholson and Carlisle, when experimenting with the newly-invented electric battery of Volta, discovered that if two gold wires connected with the copper and zinc poles of the battery are dipped into water, bubbles of oxygen and hydrogen, respectively, rise from these wires. If copper or iron wires are used, only hydrogen comes off; the oxygen is absorbed by the wire, producing an oxide. Cruickshank also collected the gases separately, and found that 2 volumes of hydrogen and 1 volume of oxygen were liberated. This agrees with Cavendish's result of the synthesis of water. Davy in 1806 showed that if very pure water is electrolysed in a gold vessel, and the experiment carried out in a vacuum receiver, so that no impurities can enter from the air, or be dissolved from



glass or other substances of ordinary vessels, then nothing but hydrogen and oxygen are produced. Thus water is decomposed by the electric current into hydrogen and oxygen in the ratio of 2 to 1 by volume.

An apparatus for the decomposition of water by the current, or the electrolysis of water, is shown in Fig. 97. It is called a **voltameter** or **coulometer**, and consists of two graduated glass tubes, with stopcocks above, connected by a horizontal tube, carrying a funnel for filling the apparatus with dilute sulphuric acid.\* The electrodes for leading the current into and out of the liquid consist of pieces of platinum foil.

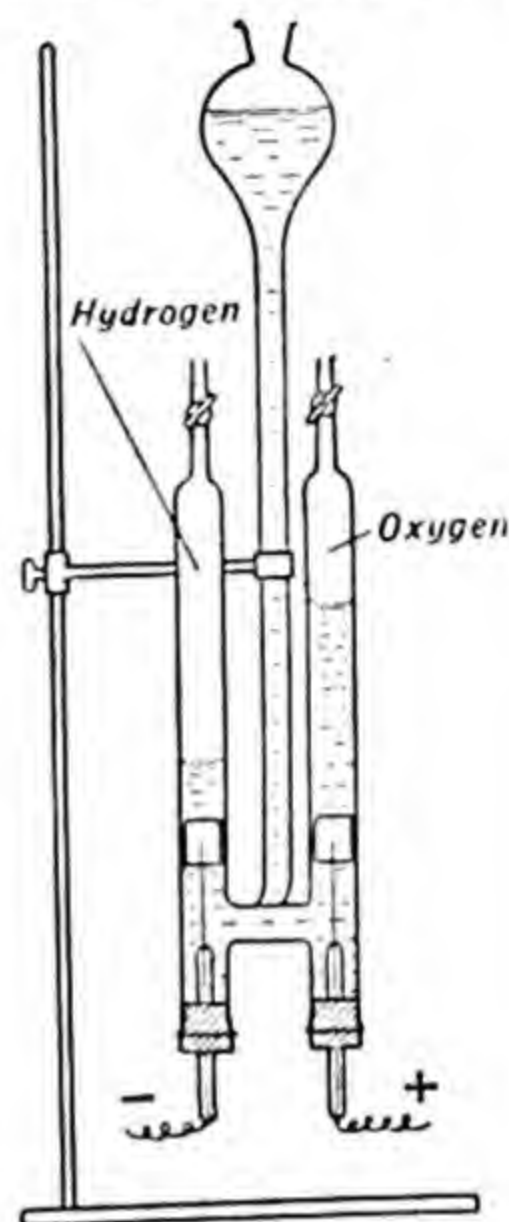


FIG. 97.—DECOMPOSITION OF WATER INTO HYDROGEN AND OXYGEN BY ELECTROLYSIS.

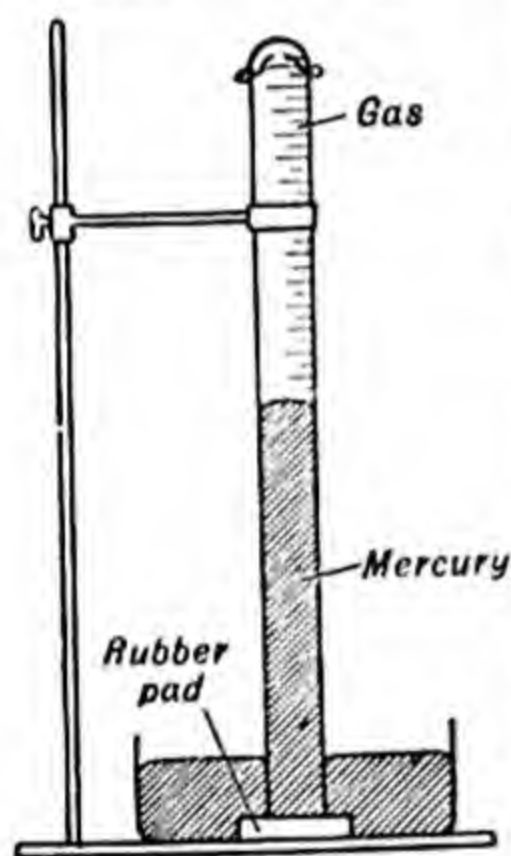


FIG. 98.—BUNSEN'S EUDIOMETER, FOR EXPLoding A MIXTURE OF GASES CONFINED OVER MERCURY.

Bubbles of gas rise from each electrode; that coming from the positive wire, although it appears more abundant because it is liberated in smaller bubbles, will be found to occupy half the volume of the other gas, and, if allowed to escape

from the tap on to a glowing chip of wood, will rekindle the latter. This gas is oxygen. The other gas, evolved from the negative wire, when ignited by a taper, burns with a blue flame, and is hydrogen. Thus, water is decomposed by electrolysis into 2 volumes of hydrogen + 1 volume of oxygen.

#### Synthesis of water in the eudiometer.—

A Bunsen's eudiometer (Fig. 98), consisting of a strong graduated glass tube, sealed at one end and provided with two platinum wires sealed through the glass for the purpose of passing an electric spark, is used. It is filled with mercury and inverted over that liquid in a trough. Pure hydrogen is

\* Pure water is almost a non-conductor of electricity, but it allows the current to pass when a little acid is added. Only the water is decomposed.

then passed in and the volume accurately read off, the corrections for temperature and pressure being applied (p. 119). Suppose the corrected volume is 28.4 c.c. A volume of pure oxygen, less than half that of the hydrogen, is now added.

Suppose the *total* corrected volume is now 39.2 c.c. The volume of oxygen is, therefore,  $39.2 - 28.4 = 10.8$  c.c.

The open end of the eudiometer is now held down firmly on a pad of rubber beneath the mercury, and an electric spark from a coil is passed. There is a flash of light in the tube and a dull noise is heard. Drops of water appear on the walls of the tube after cooling.

The eudiometer is, after cooling, lifted from the rubber pad, and the remaining volume of hydrogen read off and corrected for temperature and pressure. It should be found to be 6.8 c.c. Thus,  $28.4 - 6.8 = 21.6$  c.c. of hydrogen have combined with 10.8 c.c. of oxygen, or the two gases have combined in the ratio of 2 volumes of hydrogen to 1 volume of oxygen. That the residual gas is hydrogen may be confirmed by testing it with a taper. This result confirms that found by electrolysis.

We have still to find *the volume of steam* produced from the combination of the gases, if it were kept gaseous. It is then most convenient to measure the volumes of all the gases at some *constant* temperature, higher than the condensing point of steam.

By using a U-shaped eudiometer, the graduated limb of which is surrounded by a glass jacket through which the vapour of boiling amyl alcohol ( $131^{\circ}$ - $132^{\circ}$ ) is passed, the water produced by the explosion is kept in the form of vapour (Fig. 99). Twenty c.c. of hydrogen and 10 c.c. of oxygen are introduced, measured at the temperature of the jacket, with the mercury levels adjusted to equality on both sides by lowering the mercury reservoir. The open end of the U-tube is firmly closed by the thumb, and a spark passed from the coil. There is a flash of light, and an immediate contraction. By running mercury into

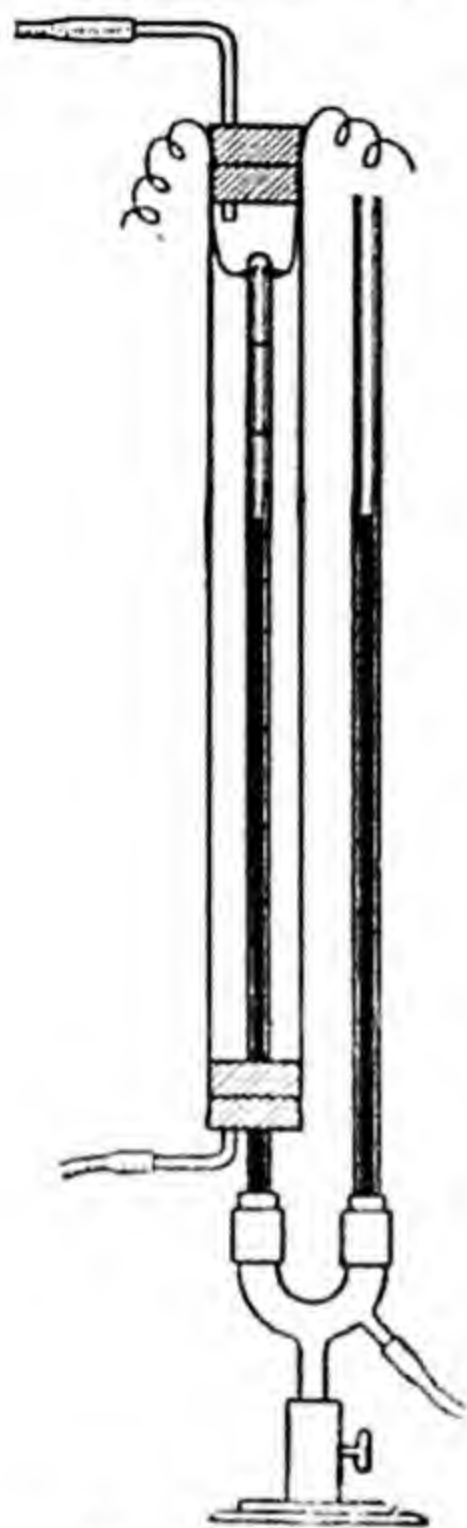


FIG. 99. — THE VOLUMETRIC COMPOSITION OF STEAM.



the open limb until the levels are again equal, it will be seen that the residual steam occupies 20 c.c. The 30 c.c. of gas contained, as we know, 20 c.c. of hydrogen and 10 c.c. of oxygen, hence :

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

**The composition of water by weight.**—Since it is difficult to weigh with accuracy large volumes of hydrogen and oxygen, the composition of water by weight (or the *gravimetric* composition) may be found by an indirect method. A stream of dry hydrogen, which is not weighed, is passed over weighed copper oxide (prepared by heating copper turnings in air) heated to dull redness. The oxide is *reduced* by the hydrogen to metallic copper, the oxygen of the oxide uniting with the hydrogen to form water, which is collected in a weighed calcium chloride tube and weighed. From these results we find :

Loss of weight of copper oxide = weight of oxygen =  $o$  ;

Weight of water – weight of oxygen = weight of hydrogen =  $h$  ;

$\therefore$  ratio of combining weights =  $o/h$ .

The apparatus is shown in Fig. 100. This method was used by Berzelius and Dulong, and the experiment was repeated,

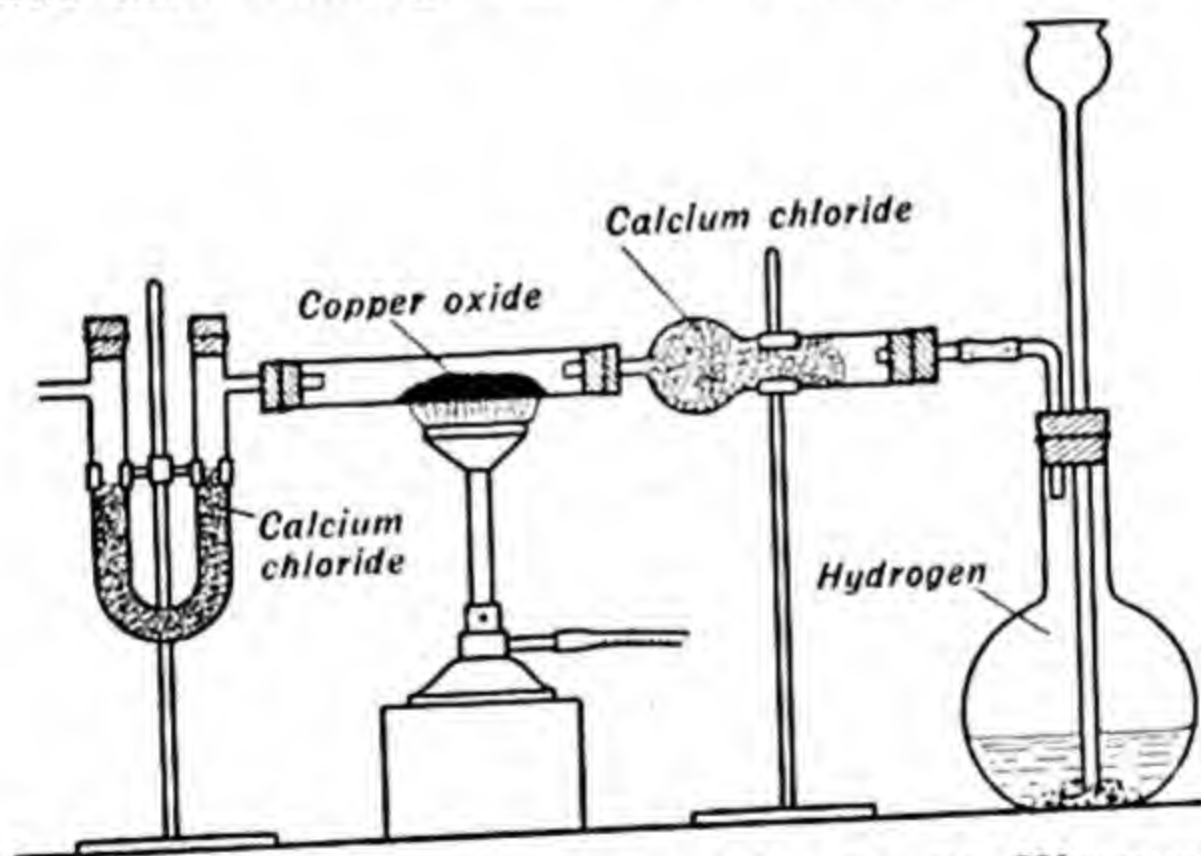


FIG. 100.—COMPOSITION OF WATER BY WEIGHT.

HYDROGEN GENERATED IN THE FLASK IS DRIED BY CALCIUM CHLORIDE AND PASSED OVER HEATED COPPER OXIDE. THE WATER VAPOUR IS COLLECTED IN A CALCIUM CHLORIDE TUBE.

with an improved apparatus, by Dumas in 1842. The hydrogen, generated from zinc and dilute sulphuric acid, was carefully purified and dried in the manner explained in Fig. 101. The

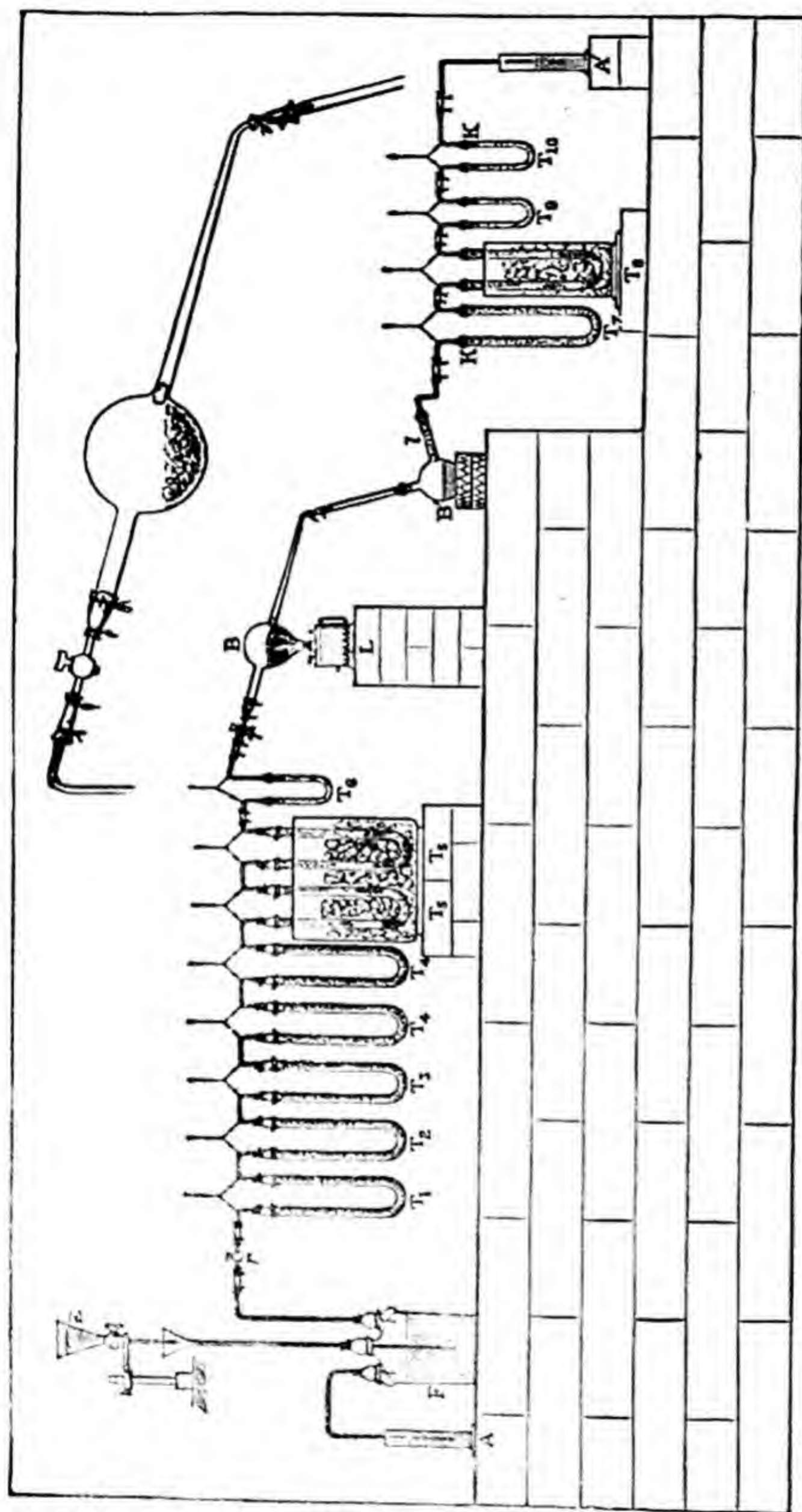


FIG. 101.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

F, A Woulfe's bottle for the generation of hydrogen; E, a tap-funnel containing sulphuric acid; A, a mercury safety-valve; T<sub>1</sub>, a tube containing lead nitrate spread on broken glass; T<sub>2</sub>, a tube containing glass moistened with silver sulphate; T<sub>3</sub>, a tube containing (a) pumice soaked in potash solution, (b) solid potash; T<sub>4</sub>, T<sub>5</sub>, tubes containing pieces of potash; T<sub>6</sub>, T<sub>7</sub>, tubes containing phosphorus pentoxide (or sometimes sulphuric acid spread over pumice), cooled in a freezing mixture; T<sub>8</sub>, a 'témoin' tube containing phosphorus pentoxide and pumice; B, the bulb (shown above on a larger scale) containing copper oxide, with stopcock and pointed tube delivering into the receiver, B', for collecting the water, with fragments of calcium chloride at I; L, a large spirit lamp for heating the bulb; T<sub>9</sub>, a tube of solid potash; T<sub>10</sub>, a tube of phosphorus pentoxide (or sulphuric acid on pumice), cooled in a freezing mixture; T<sub>11</sub>, a 'témoin' tube of phosphorus pentoxide; T<sub>12</sub>, a guard-tube of phosphorus pentoxide (not weighed) to exclude moisture; A', escape-valve for excess of hydrogen, containing sulphuric acid.



lead nitrate removed sulphuretted hydrogen, the silver sulphate removed arseniuretted hydrogen, the caustic potash removed acid vapours and moisture, and the sulphuric acid or phosphorus pentoxide removed water vapour.

The copper oxide was contained in a large hard glass bulb with a long neck. This was weighed after evacuation to remove the air. The air was displaced from the apparatus by hydrogen, and the bulb heated by a large spirit lamp for ten to twelve hours. The water produced was collected in a smaller bulb, in the neck of which calcium chloride was placed, followed by a series of four drying tubes containing sulphuric acid on pumice, or phosphorus pentoxide. The last tube communicated with a vessel of sulphuric acid, through which the residual hydrogen escaped. In all the experiments the weight of the last absorption tube was constant.

The copper was allowed to cool in the bulb in a stream of hydrogen, the hydrogen was displaced by air in the whole apparatus, and the bulb then exhausted and weighed. The absorption system was also weighed.

A mean of nineteen experiments gave the following result :

	Percentage by weight.	Combining ratio by weight.
Oxygen - - -	88.864	7.98
Hydrogen - - -	11.136	1.00
	<hr/> 100.000	<hr/> 8.98

This ratio was accepted without question for nearly half a century. Dumas himself, however, had pointed out two sources of error in the method :

(1) Air dissolved in the sulphuric acid passed on with the hydrogen, and the oxygen of this air combined with hydrogen in the copper oxide bulb ;

(2) The reduced copper retained hydrogen when cooled in that gas.

Both errors tended to reduce the loss of weight of the bulb, so that the proportion of oxygen found would be too small. Dumas thought the ratio should be exactly 8 of oxygen to 1 of hydrogen ; we now know that it is very nearly 7.94 of oxygen to 1 of hydrogen.

The most exact experiments on the composition of water by weight are those of the American chemist, E. W. Morley, carried

out from 1880 to 1895. Purified oxygen and hydrogen gases were weighed in large glass globes; in the later experiments the hydrogen was weighed in a bulb containing palladium, a



FIG. 102.—MORLEY'S COMBUSTION TUBE.

THE DRY GASES PASSED THROUGH PHOSPHORUS PENTOXIDE TUBES, *b, b*, TO THE JETS, *a, a*, WHERE THEY WERE IGNITED BY ELECTRIC SPARK BETWEEN WIRES FROM THE ELECTRODES, *f* AND *f*.

metal of the platinum group which has the unique property of absorbing large volumes of hydrogen, but not other gases. When the palladium charged with hydrogen is strongly heated pure hydrogen is evolved. The gases were burnt at platinum jets in a previously evacuated sealed glass vessel (Fig. 102), immersed in cold water. The water was then frozen, and the residual gas pumped out through a tube containing phosphorus pentoxide (to keep back water vapour), and analysed.

As a final result, the mean of twelve experiments in which 400 gm. of water were produced, Morley obtained the ratio:

$$\text{Oxygen : hydrogen} :: 7.9396 : 1$$

The weight of hydrogen combining with 8 parts by weight of oxygen is therefore 1.00762, and this is the atomic weight of hydrogen (p. 138), since two atoms of hydrogen combine with one of oxygen, of weight 16. The accepted value of this is now taken as 1.0080, which agrees better with the results of another American experimenter, W. A. Noyes (1907). He weighed

palladium charged with hydrogen in a vacuum tube, heated the tube, and admitted pure oxygen to burn the hydrogen. The water formed was condensed in a cooled extension of the tube. The increase in weight of the tube gave the weight of oxygen admitted. The residual gas was pumped out and analysed, and the water transferred by evaporation to another tube and weighed. The best results gave  $H = 1.00787$ .



## CHAPTER VII

### THE PHYSICAL PROPERTIES OF GASES

**Boyle's law.**—The pneumatic tyres of bicycles and motor cars contain air under pressure. In order to force air into the tyre a pump is used, and it is clear that when air is made to occupy a smaller volume than it does under the normal pressure of the atmosphere, an additional pressure must be applied to it.

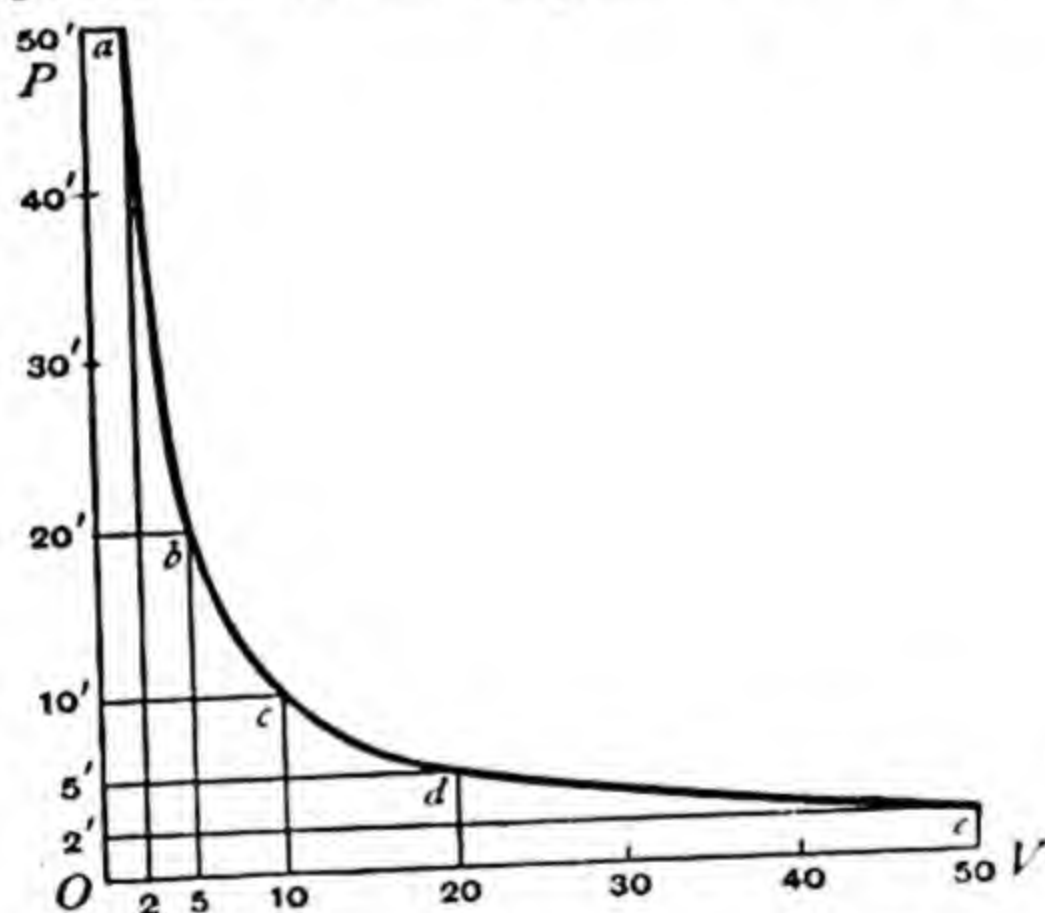


FIG. 103.—BOYLE'S LAW CURVE.

THE AREAS *a*, *b*, *c*, *d* AND *e* ARE ALL EQUAL TO 100 SQUARE UNITS, SINCE  
 $\text{pressure} \times \text{volume} = \text{CONSTANT}.$

The volume of air (or any other gas) also changes when the temperature is changed, and it depends to some extent on the amount of moisture in the gas. In accurate experiments it is therefore necessary to say at what pressure and temperature the volume is measured, and whether the gas is dry or not.

In practice all gaseous volumes, no matter what are the conditions in which they are measured, are always reduced by calculation to the volume the gas would occupy if it were

(a) dry ; (b) at a temperature of  $0^{\circ}\text{C.}$ , and (c) under a pressure of 760 mm. of mercury. The conditions  $0^{\circ}\text{C.}$  and 760 mm. pressure are called *standard* (or normal) *temperature and pressure* generally written as S.T.P. (or N.T.P.). The pressure 760 mm. is chosen because it is about the average barometric pressure.

To perform this calculation we must first know how the volume of a gas varies with the pressure when the temperature is constant. This was found experimentally by Boyle in 1662 and the result is called **Boyle's law** :

The volume of a given mass of gas at constant temperature is inversely proportional to the pressure.

The graph in Fig. 103 also shows that Boyle's law may be stated in the form that, at constant temperature :

$$\text{pressure} \times \text{volume} = \text{constant} ;$$

$$P_1V_1 = P_2V_2.$$

**Expansion of gases by heat.**—We next require the effect of change of temperature on the volume of a gas at constant pressure. This is given by a law stated by Gay-Lussac and by Dalton in 1801 but often called **Charles's law**. It states that : if the pressure is constant, a volume of a given mass of gas expands by  $\frac{1}{273}$  of its volume at  $0^{\circ}\text{C.}$  for each  $1^{\circ}\text{C.}$  rise in temperature.

Let  $V_0$  be the volume at  $0^{\circ}\text{C.}$  The expansion due to a rise in temperature of  $t^{\circ}\text{C.}$  will be  $\frac{tV_0}{273}$  and the volume at  $t^{\circ}\text{C.}$  will be

$$V_t = V_0 + \frac{tV_0}{273} = V_0 \left( 1 + \frac{t}{273} \right) = V_0 \cdot \frac{273 + t}{273}.$$

When  $t = -273$  the volume is zero, so that if a gas continued to contract at the same rate on cooling to  $-273^{\circ}\text{C.}$  it would

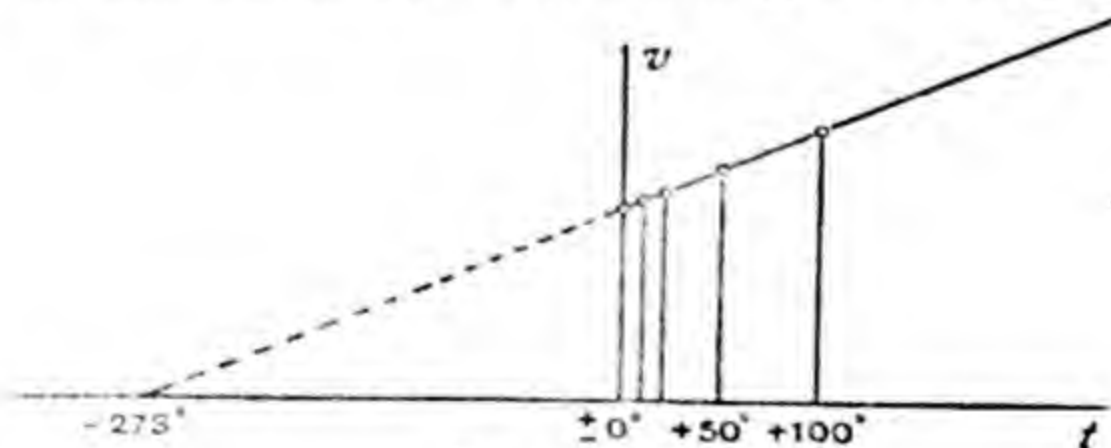


FIG. 104.

CURVE SHOWING VOLUMES OF A GAS AT VARIOUS TEMPERATURES. WHEN EXTRAPOLATED TO  $-273^{\circ}\text{C.}$  THE VOLUME BECOMES ZERO.

occupy no volume at that temperature, which is called the **absolute zero** (Fig. 104). Actually the gas would become liquefied



before this temperature was reached. If we reckon temperature from  $-273^{\circ}\text{C.}$  as zero we obtain the absolute temperature, denoted by  $T$ .

Thus,  $0^{\circ}\text{C.} = 273^{\circ}\text{abs.}$ , and  $t^{\circ}\text{C.} = (t + 273)^{\circ}\text{abs.}$

If  $V_1, V_2$  are the volumes of a gas at  $t_1^{\circ}\text{C.}$  and  $t_2^{\circ}\text{C.}$  the equation above shows that

$$\frac{V_2}{V_1} = \frac{V_0(273 + t_2)}{273} \cdot \frac{273}{V_0(273 + t_1)} = \frac{t_2 + 273}{t_1 + 273} = \frac{T_2}{T_1},$$

that is to say, the volume of a given mass of gas at constant pressure is proportional to the absolute temperature.

**Examples of calculations of gaseous volumes:**

*Example 1.*—A volume of gas occupies 224 c.c. under a pressure of 755 mm. What will be its volume under a pressure of 760 mm. if the temperature remains constant?

We use Boyle's law: pressure  $\times$  volume = constant;

$$\therefore 755 \times 224 = 760 \times x,$$

or

$$x = 224 \times \frac{755}{760} = 222.5 \text{ c.c.}$$

*Example 2.*—The volume of a gas at  $16^{\circ}$  is 450 c.c. What will be the volume at  $0^{\circ}$  if the pressure remains constant?

We use Charles's law:  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ ;

$$T_1 = 273 + 16 = 289; \quad V_1 = 450 \text{ c.c.};$$

$$T_2 = 273 + 0 = 273; \quad V_2 = x;$$

$$\therefore \frac{450}{289} = \frac{x}{273}, \text{ or } x = 450 \times \frac{273}{289} = 425.1 \text{ c.c.}$$

*Example 3.*—A volume of gas at  $15^{\circ}\text{C.}$  and 750 mm. is 4.5 litres. Find the volume at S.T.P.

Suppose the pressure changed from 750 mm. to 760 mm. whilst the temperature remains constant at  $15^{\circ}\text{C.}$  The volume will become:

$$4.5 \times \frac{750}{760} \text{ litres.}$$

Now let the pressure remain constant at 760 mm. and change the temperature from  $15^{\circ}\text{C.}$  to  $0^{\circ}\text{C.}$  The volume becomes:

$$\left(4.5 \times \frac{750}{760}\right) \times \frac{273}{289} = 4.196 \text{ litres.}$$

Generally, let  $V_1, P_1, T_1$  and  $V_2, P_2, T_2$  be the corresponding volumes, pressures and *absolute* temperatures. Then :

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This formula will enable all problems of this type to be solved.

**Partial pressures.**—In a mixture of two (or more) gases we may consider the total pressure exerted by the gas to be the sum of the partial pressures of each gas. The partial pressure is the pressure each gas would exert if it were separately confined in the *whole volume occupied by the mixture*. This result is called Dalton's law of partial pressures, and it is established by experiment.

The partial pressures can be calculated by Boyle's law when we know the composition of the mixture. For example, air contains one volume of oxygen and four volumes of nitrogen. Let us imagine that a certain volume of air is confined in a globe at a pressure of 1 atmosphere. Now suppose the oxygen could be removed (say by exposing phosphorus to the air in the globe), then the pressure will fall by the amount of the partial pressure of the oxygen. This is the pressure which the oxygen would exert if it alone were present in the globe and, by Boyle's law, is one-fifth of an atmosphere. The pressure of the nitrogen is, by similar reasoning, four-fifths of an atmosphere. The sum of the partial pressures is :

$$\frac{1}{5} \text{ atm. for the oxygen} + \frac{4}{5} \text{ atm. for the nitrogen} \\ = 1 \text{ atm. for the mixture.}$$

**Correction for moisture in a gas.**—In accurate work a correction must be applied to the volume of a gas *measured over water* in order to find the true volume which the gas would occupy if dry.

If water evaporates into a dry gas at constant pressure, the gas will expand. The volume of a given mass of gas is therefore *greater* when it is moist than when it is dry.

Suppose we have a volume of 100 c.c. of moist air, measured over water at  $15^\circ$ , and under a total pressure of 760 mm. This total pressure is the sum of the pressure of the dry air and of the maximum pressure of water vapour at  $15^\circ$ , viz. 12.7 mm. The pressure of the *dry* air is therefore  $760 - 12.7 = 747.3$  mm. If the water vapour were removed by a drying agent from the 100 c.c. of moist air contained in a closed vessel, the pressure would therefore fall to 747.3 mm. If we now increased the



pressure of the dry air to 760 mm., the volume would become, by Boyle's law,  $100 \times \frac{747.3}{760}$  c.c., and at  $0^\circ$  this would be

$$100 \times \frac{747.3}{760} \times \frac{273}{288} = 93.2 \text{ c.c.}$$

If we had omitted to correct for moisture, the volume at S.T.P. would have been

$$100 \times \frac{273}{288} = 94.8 \text{ c.c.}$$

The error, 1.5 c.c., would scarcely be appreciable in elementary work, but it is large when the volumes are accurately measured.

If a mass of *moist* gas occupies a volume  $V$  at a temperature  $t$  under a total pressure  $P$ , the volume of *dry* gas at S.T.P. will be

$$V \times \frac{P-f}{760} \times \frac{273}{273+t},$$

where  $f$  is the partial pressure of water vapour in the moist gas. If the gas is *saturated* with moisture,  $f$  is the maximum pressure of water vapour at the temperature  $t$ , as given in the tables of vapour pressures.

**Density of a gas.**—The comparative 'heaviness' of solids and liquids is measured by weighing equal volumes of them, and when the volume is unit volume, usually 1 c.c., the weights measure the densities. Another method is to divide the weight of a certain volume of the solid or liquid by the weight of an *equal volume of water* (taken as a standard liquid), when we obtain the *specific gravity*. Now gases are very light, so that the weight of 1 c.c. would be inconveniently small, and also they are so very much less dense than water that this would not be a convenient standard of comparison. It is usual, therefore, to take somewhat different definitions of density and specific gravity (or *relative density*) in the case of gases, or vapours.

(1) The **normal density**, or simply **density**, of a gas is the weight in grams of 1 litre measured at a temperature of  $0^\circ$ , and under a pressure of 760 mm. of mercury.

(2) The **relative density** (sometimes called **vapour density**) of a gas or vapour is the weight of any volume divided by the weight of an *equal volume of hydrogen* at the same temperature and pressure. Hydrogen is taken as the standard because it is the lightest gas known.

**Determination of gas densities.**—The density of a gas is determined by weighing an evacuated globe, filling it with the gas, and reweighing. The volume of the globe is determined by filling it with water and reweighing.

If the globe is weighed first vacuous, then full of the gas, and finally filled with hydrogen under the same conditions, the relative density is given by :

$$\frac{\text{weight of gas filling globe}}{\text{weight of hydrogen filling globe.}}$$

One litre of hydrogen at S.T.P. weighs 0.09 gram.

In an experiment the weight of the vacuous globe was 148.56 gm. and its volume was 980 c.c. When filled with carbon dioxide at 15° and 758 mm. pressure the globe weighed 150.38 gm. The weight of the carbon dioxide was, therefore, 1.82 gm. Its volume at S.T.P. is

$$980 \times \frac{758}{760} \times \frac{273}{288} = 926.5 \text{ c.c.}$$

hence the weight of 1 litre at S.T.P. is

$$\frac{1.82 \times 1000}{926.5} = 1.96,$$

which is the normal density of carbon dioxide.

The weight of 1 litre of hydrogen at S.T.P. = 0.09 gm. ;

∴ the relative density of carbon dioxide is  $\frac{1.96}{0.09} = 22.$

**\*Determination of vapour densities.**—Two methods of determining the relative density of the vapour of a volatile liquid are commonly used.

In Victor Meyer's method a long glass tube with a bulb (Fig. 105) and a side tube is heated in a vapour bath at a temperature which must be constant and higher than the boiling point of the substance, but need not otherwise be known. The side tube delivers into a graduated tube in a trough of water. The long tube is heated in the bath until no more bubbles of air escape ; then the side tube is placed under the graduated tube, the cork at the top of the long tube is taken out, and a weighed quantity of the liquid in a small stoppered bulb dropped into the heated bulb, the cork being quickly replaced. A little mercury is placed in the bottom of the bulb to prevent fracture on dropping in the bulb of liquid.



The substance quickly vaporises, and the vapour (which does not diffuse to the top of the narrow tube) displaces its own volume of air, which is collected in the graduated tube. When no more bubbles come off, the volume of air is read off and corrected for pressure and temperature.

*Example.*—0.1008 gm. of chloroform expelled 20.0 c.c. of air at 15° and 757 mm. pressure.

∴ volume of air at S.T.P.

$$= 20 \times \frac{273}{288} \times \frac{757}{760} = 18.9 \text{ c.c.}$$

Weight of an equal volume of hydrogen = 18.9 × 0.00009 gm. = 0.001701 gm. ;

∴ vapour density of chloroform = 0.1008 / 0.001701 = 59.3.

In Dumas' method a glass bulb (Fig. 106) with a long neck is dried and weighed. By warming the bulb, dipping the neck in the liquid, and cooling, sufficient liquid is introduced into the bulb to expel all the air when it is volatilised.

The bulb is then supported in an iron pot containing water, oil, or melted paraffin wax, heated above the boiling point of the liquid. Volatilisation rapidly occurs, the air being expelled through the tip of the bulb, which projects above the surface of the liquid in the bath. When the rush of vapour ceases, the neck of the globe is sealed off, and the temperature of the bath read off on the thermometer. The globe is removed from the bath, cooled, cleaned, and reweighed along with the

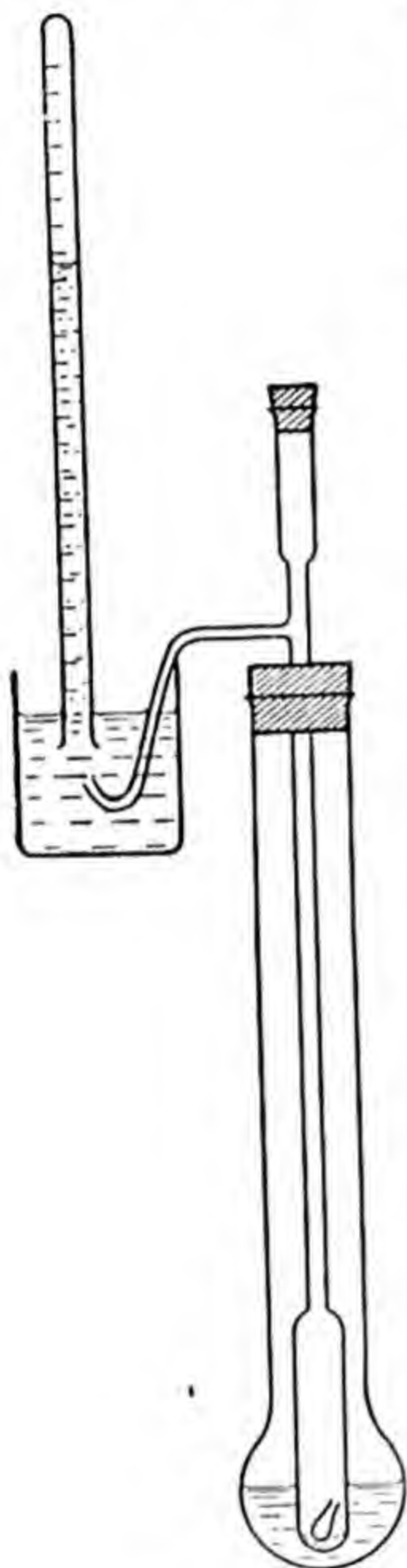


FIG. 105.

VICTOR MEYER'S VAPOUR DENSITY APPARATUS.

piece of neck sealed off. The neck is then scratched with a file, and the tip broken off under water. The latter rushes into the

bulb and fills it completely. The bulb full of water is weighed, together with the two small pieces of the neck. The barometric

pressures during the second weighing, and at the time of sealing, are noted.

The following example shows the method of calculation :

*Vapour density of hexane.*

Weight of empty globe  
in air = 23.449 gm.

Weight of globe + vapour  
at  $15.5^{\circ}$  = 23.720 gm.

Temperature of sealing  
=  $110^{\circ}$ .

Barometric pressure  
= 759 mm.,  
unchanged throughout the  
experiment.

Capacity of globe, by  
weighing water  
= 178 c.c.

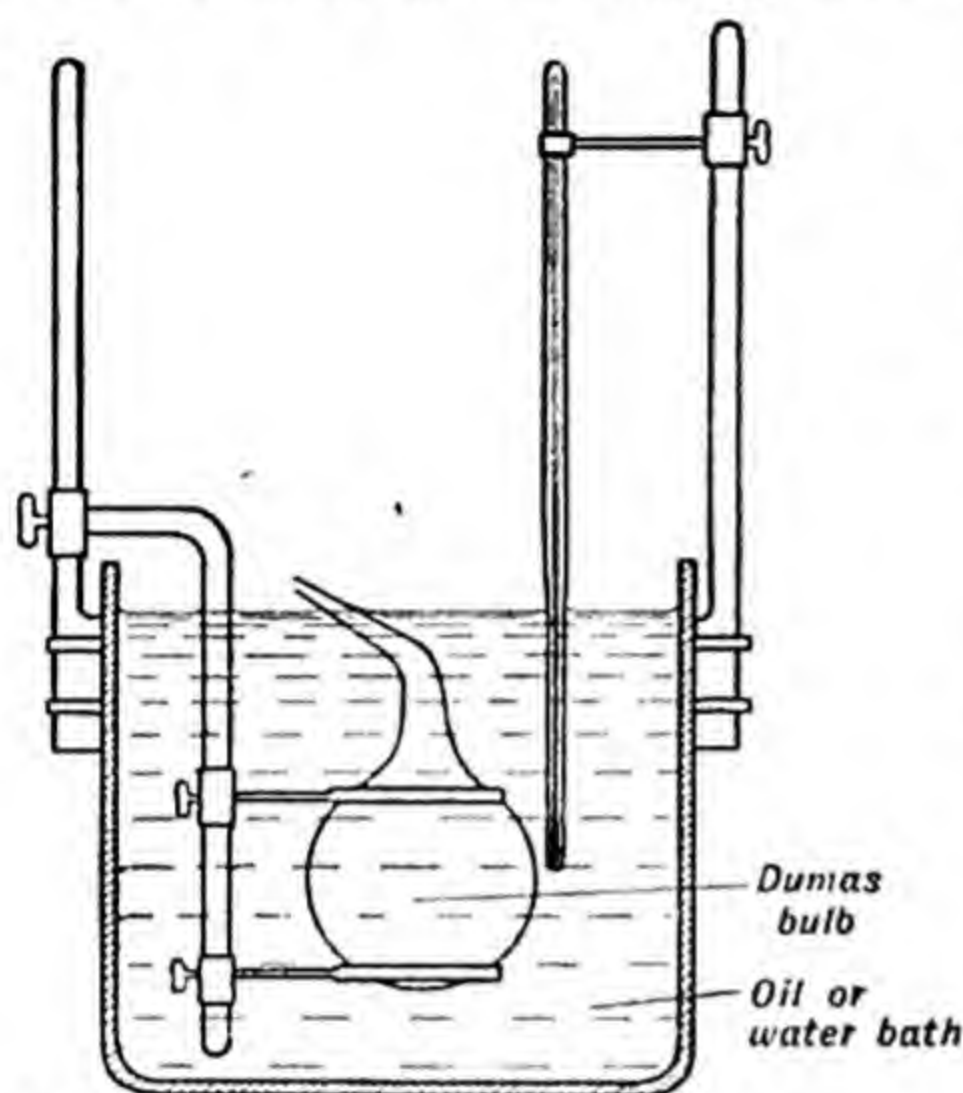


FIG. 106.—DUMAS' VAPOUR DENSITY APPARATUS.

Weight of air displaced by globe

$$= 178 \times \frac{273}{288.5} \times \frac{759}{760} \times 0.001293 = 0.218 \text{ gm.}$$

(0.001293 gm. is the weight of 1 c.c. of air at S.T.P.)

Weight of *vacuous* globe =  $23.449 - 0.218 = 23.231$  gm.

$\therefore$  weight of vapour filling globe at  $110^{\circ}$  and 759 mm.  
=  $23.720 - 23.231 = 0.489$  gm.

Weight of hydrogen filling globe at  $110^{\circ}$  and 759 mm.

$$= 178 \times \frac{273}{383} \times \frac{759}{760} \times 0.00009 = 0.0114 \text{ gm.}$$

(0.00009 gm. is the weight of 1 c.c. of hydrogen at S.T.P.) ;

$\therefore$  vapour density of hexane =  $0.489 / 0.0114 = 42.9$ .

The vapour densities are shown later to be of great importance in the determination of molecular weights and atomic weights.



## CHAPTER VIII

### THE LAWS OF CHEMICAL COMBINATION

**The law of constant proportions.**—As a result of a large number of experiments on the analysis of compounds, both those occurring in Nature as minerals and those prepared in the



FIG. 107.—JOSEPH LOUIS PROUST, 1754-1826.

laboratory, the French chemist Proust, who was professor in Madrid, was led in 1799 to the following generalisation, which is called the law of constant proportions :

When combination between elements takes place, it is always in

definite proportions by weight, so that the composition of a pure chemical compound is always the same.

This means, for example, that red mercury oxide always has the same composition, 100 parts of mercury to 8 parts of oxygen, by weight; water is always composed of 1 part of hydrogen and 8 parts of oxygen, by weight, and so on. The substances are, of course, supposed to be pure.

The French chemist, Claude Louis Berthollet (1748-1822), who accompanied Napoleon on his expedition to Egypt, believed that the composition of a chemical compound could vary, partly owing to variation in the method by which it was prepared. Most of the examples which Berthollet brought forward were shown by Proust to be *mixtures* in varying proportions of two or more compounds, each of definite composition.

The existence of isotopes (p. 239) complicates the law of definite proportions somewhat, since in one case, viz. lead, it has been found that the compounds may differ appreciably in composition. There are different varieties (isotopes) of the element lead. The same holds for some other elements, e.g. chlorine, but in most cases the mixture of isotopes which was formerly regarded as a simple element always occurs in Nature in the same proportions. Since the isotopes of an element have the same chemical properties, it follows that the compounds formed from the isotopic mixture will always have the same composition.

**Isomerism and allotropy.**—The law of constant proportions asserts that a definite compound has a fixed chemical composition. The converse is not always true: the same elements, combined in the *same* proportions by weight, may form two or more different substances, with characteristic physical and chemical properties. This property is known as **isomerism**, and the different substances of the same composition are called **isomers**. Chemical composition alone does not uniquely determine a pure substance; even elements may exist in **allotropic** modifications (p. 56).

**The law of multiple proportions.**—As a result of theoretical speculations, John Dalton, in 1803, was led to assume that: if two elements combine to form more than one compound, the weights of one element which unite with identical weights of the other are in simple multiple proportion.

Although Proust was acquainted with different oxides of each of the metals, tin, copper, and iron, his analyses were not sufficiently accurate to disclose any simple relation between the



weights of oxygen combined with identical weights of metal or *vice versa*.

There are two oxides of copper, one a black and the other a red solid. These may be analysed by reducing known weights of each oxide to the metal by heating in a current of hydrogen, when water is also formed, as described on p. 113. The loss in weight of the solid gives the oxygen, and the residual copper is weighed at the same time. It is then found that the percentage compositions of the two oxides are as follows :

		Black oxide	Red oxide
Copper	-	79.9	88.8
Oxygen	-	20.1	11.2

Now, let the weights of copper be found which combine with a *fixed* weight of oxygen, say 11.2 parts. These are 88.8 for the red oxide and  $79.9 \times 11.2 \div 20.1 = 44.4$  for the black oxide. We now see at once that in the red oxide the weight of copper which combines with a fixed weight of oxygen is exactly twice that in the black oxide.

The most striking example of the law of multiple proportions is furnished by the five oxides of nitrogen. The percentage compositions by weight of these five compounds are as follows :

	Nitrous oxide.	Nitric oxide.	Nitrous anhydride.	Nitrogen dioxide.	Nitric anhydride.
Nitrogen	63.7	46.7	36.9	30.5	25.9
Oxygen	36.3	53.3	63.1	69.5	74.1

The weights of oxygen combined with 100 parts of nitrogen in these compounds are found by proportion, and are as follows :

57	114	171	228	285
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If all these numbers are divided by the least, 57, we obtain the series :

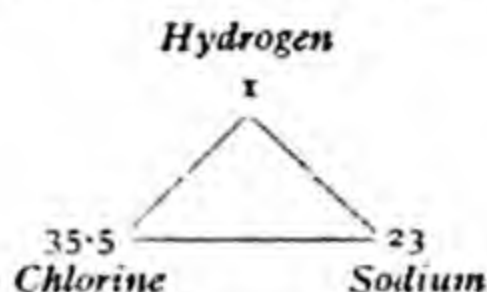
1	2	3	4	5
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Thus the weights of oxygen combining with identical weights, 100 parts, of nitrogen to form the five compounds are in the simple ratios 1 : 2 : 3 : 4 : 5.

**The law of equivalent proportions.**—It is found that 23 gm. of sodium combine with 1 gm. of hydrogen to form sodium hydride ; 35.5 gm. of chlorine combine with 1 gm. of hydrogen to form hydrogen chloride. The equivalent weights of sodium and chlorine, with respect to combination with hydrogen, are therefore 23 and 35.5, respectively. Now sodium and chlorine

also combine together to form sodium chloride, and it is found that 23 parts of sodium combine with 35.5 parts of chlorine to form sodium chloride.

Thus, *the weights of sodium and chlorine which separately combine with 1 part by weight of hydrogen are the weights in which these two elements combine with each other.* This fact may be illustrated by the annexed diagram.



The generalisation of this result was stated by Richter in 1792 and is called the **law of equivalent proportions** (sometimes the **law of reciprocal proportions**, or the **law of combining weights**) :

The weights of two or more elements, A and B, which combine separately with a fixed weight of another element, C, are either the weights in which A and B combine with one another or are simple multiples of them.

**Equivalents.**—If 23 gm. of sodium are heated in hydrogen chloride gas, it is found that 1 gm. of hydrogen is displaced, whilst 35.5 gm. of chlorine combine with the 23 gm. of sodium to form sodium chloride. Thus, 23 parts of sodium can combine with 1 part of hydrogen, and can also *displace* it from its combination with another element.

The **equivalent** of an element is that weight of it which combines with, or displaces, **1 part by weight of hydrogen.**

Hydrogen is taken as the standard because it is found that no element has an equivalent less than that of hydrogen.

The conception of an equivalent implies that, when once the equivalent of a single element has been determined with respect to hydrogen, the equivalent of that element may be used instead of hydrogen in the determination of other equivalent weights. Thus, having found that the equivalent of chlorine with respect to hydrogen is 35.5, we may use 35.5 parts of chlorine instead of 1 part of hydrogen in finding the equivalent of an element which combines with chlorine but does not combine with hydrogen. In the case of sodium, which combines with both hydrogen and chlorine, the equivalents are found to be identical. In other cases, the element may displace hydrogen but does not combine with it ; e.g., zinc, which evolves hydrogen from dilute acids,



does not form a hydride. It is again found that the weight of such an element which combines with 35.5 parts of chlorine displaces 1 part of hydrogen. In the case of elements which neither combine with nor displace hydrogen, such as gold, the equivalent weight may be determined with respect to combination with chlorine, and is thus fixed in an indirect manner. In the same way, since 8 parts of oxygen combine with 1 part of hydrogen, the equivalent of an element may be found by determining what weight of the element combines with 8 parts of oxygen.

The idea of equivalence is of fundamental importance in chemistry and no progress can be made in quantitative analysis until its meaning is thoroughly understood.

**The determination of equivalents.**—Equivalents are determined experimentally in various ways.

(1) The weight of the element combining with or displacing 1 part of hydrogen is found. This is applicable to metals which dissolve in acids, or alkalies, with evolution of hydrogen, the volume of which is measured.

(2) The weight of metal displaced from a solution of one of its salts by the equivalent of another metal, falling in class (1), is found. Thus, the equivalent of zinc is found by the measurement of the hydrogen evolved by zinc from an acid, and the equivalent of copper is then determined by weighing the copper displaced by the equivalent weight of zinc from a solution of copper sulphate.

(3) The weight of the element combining with 8 parts of oxygen is found; the combination may take place directly, as when magnesium is heated in air or oxygen, or indirectly, as when tin or copper is treated with nitric acid, and the product heated to redness. If the oxygen compound is decomposed on heating, *e.g.*, mercuric oxide, or potassium chlorate, the weight of oxygen liberated is found, and the equivalent of mercury or of potassium chloride so determined.

(4) Since 108 parts of silver combine with 35.5 parts of chlorine, the weight of silver, in the form of silver nitrate, required to precipitate the chloride of another metal will give the equivalent of the latter. For example, 108 parts of silver precipitate 74.5 parts of potassium chloride. Now, we know from the analysis of potassium chloride that this contains 52.3 per cent. of potassium. Hence the equivalent of potassium is

$$52.3 \times 74.5 \div 100 = 39.$$

Since elements sometimes combine in more than one

proportion, it follows that an element may have more than one equivalent. The law of multiple proportions then shows that the different equivalents of an element are related in simple multiples. Thus, carbon forms two compounds with oxygen, containing, for 8 parts of oxygen, 3 and  $3 \times 2$  parts of carbon, respectively.

**Equivalent weights of compounds.**—The idea of equivalence is just as applicable to compounds as it is to elements; in fact, historically, the equivalents of compounds (acids and bases) were the first to be recognised. Cavendish in 1766 and 1788 published memoirs in which he showed that the ratio of quantities of two acids which neutralised identical weights of one alkali, was the ratio of the quantities which also neutralised identical weights of another alkali, and he called these weights *equivalents*. In an unpublished research we find Cavendish weighing out equivalent weights of acids and salts, dissolving them in equal volumes of water, and finding the electrical conductivities of the solutions.

A solution which contains the equivalent weight in grams of a substance dissolved in 1 litre is called a **normal** ( $N$ ) solution. Similarly, a **decinormal** ( $N/10$ ) solution contains one-tenth of the equivalent weight in grams per litre, and so on.

We have seen above that 35.5 parts of chlorine combine with 1 part of hydrogen, hence 36.5 will be the equivalent of hydrochloric acid. A solution containing 36.5 grams of hydrochloric acid per litre will be a normal solution. If this is mixed with a solution of caustic soda in the correct proportions the latter will be neutralised, *i.e.*, the acidic properties of the solution of hydrochloric acid and the alkaline properties of the solution of caustic soda will disappear, and we shall obtain a solution of sodium chloride or common salt.

In order to find when the acidic or alkaline properties disappear we make use of **indicators**, which are dyes exhibiting different colours in acidic and alkaline solutions. Three common indicators, and the colours which they exhibit in acid and alkaline solutions are shown in the table below.

Indicator.	Colour in acid solution.	Colour in alkaline solution.
Litmus - -	Red	Blue
Methyl Orange -	Pink	Yellow
Phenolphthalein -	Colourless	Crimson

(Litmus in exactly neutral solution is purple.)



Suppose, for example, the solution of caustic soda is taken and a little methyl orange solution added. The colour will be yellow. The normal hydrochloric acid is now run into the soda solution from a graduated burette (Fig. 108) until the colour just changes to pink. If we know the weight of caustic soda in the solution we can now calculate how many grams we should dissolve in 1 litre so that 1 c.c. of the solution would neutralise 1 c.c. of normal hydrochloric acid. This will be found to be 40 grams, and a solution of 40 grams of caustic soda per litre is a normal solution.

By **titrating** (as the above operation is called) a solution of sulphuric acid with normal caustic soda solution, we can find the amount of sulphuric acid in 1 litre of normal solution. This is 49 grams. Thus, 36.5, 40 and 49 are the equivalents of hydrochloric acid, caustic soda, and sulphuric acid. We should find also that 49 grams of sulphuric acid contain 1 gram of hydrogen, and it is true for all acids that their normal solutions contain 1 gram of acidic hydrogen per litre (see p. 208).

It must be clearly understood that in using equivalent solutions we can save much time in calculation. For example, if we titrated 10 c.c. of a solution of nitric acid with normal caustic soda and found that it required 8.3 c.c. for neutralisation, we should proceed as follows :

10 c.c. of the given nitric acid solution = 8.3 c.c. of *N* caustic soda = 8.3 c.c. of *N* nitric acid.

Now *N* nitric acid contains 63 grams per litre ;

$\therefore$  1 c.c. = 0.063 grams nitric acid ;

$\therefore$  10 c.c. of the given solution =  $8.3 \times 0.063 = 0.523$  grams of nitric acid. We note that the equivalent of caustic soda does not enter the calculation at all.

**Determination of equivalents in the laboratory.**—We may now explain how equivalents of metals are determined in the laboratory. There are four principal methods.

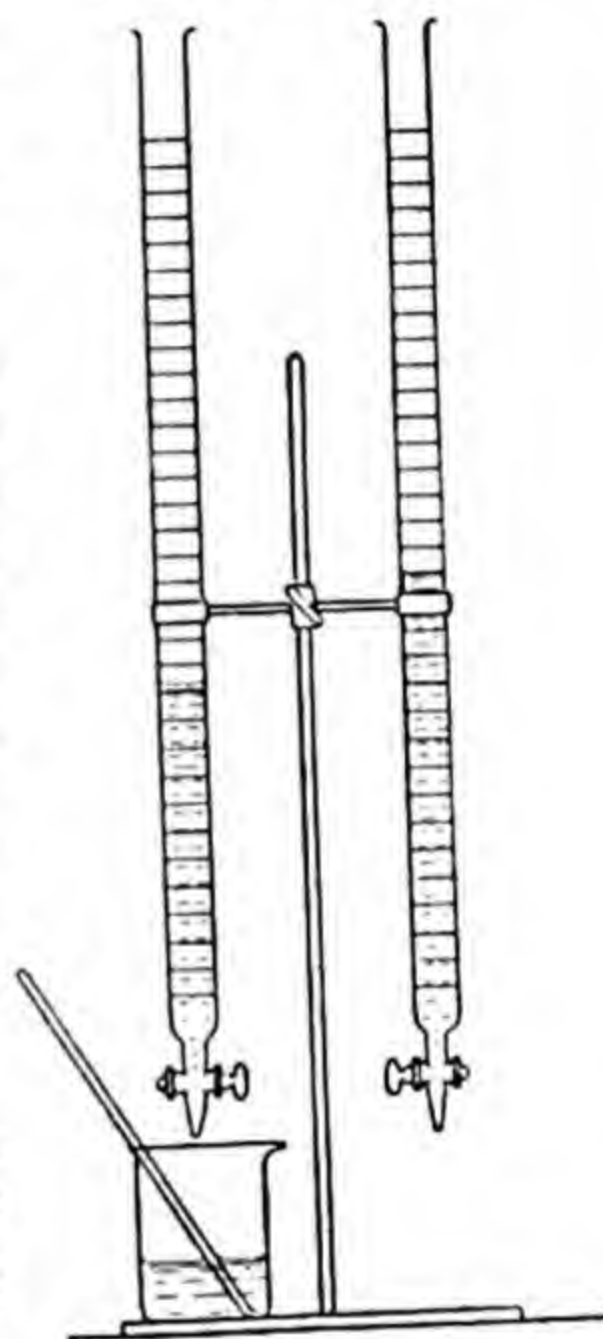


FIG. 108.—BURETTES AND APPARATUS FOR TITRATION.

*Method 1.*—A metal which dissolves in dilute acid (or alkali) with evolution of hydrogen. The metals, zinc, iron, calcium and magnesium dissolve in cold dilute hydrochloric acid with evolution of hydrogen. Aluminium dissolves in a mixture of equal volumes of concentrated hydrochloric acid and water or in warm dilute caustic soda solution. Tin dissolves in *hot* concentrated hydrochloric acid.

The apparatus used is shown in Fig. 109. About 1 gram of metal is weighed out into the small tube *A* and lowered carefully into the acid or alkali in the flask *B*, care being taken that the

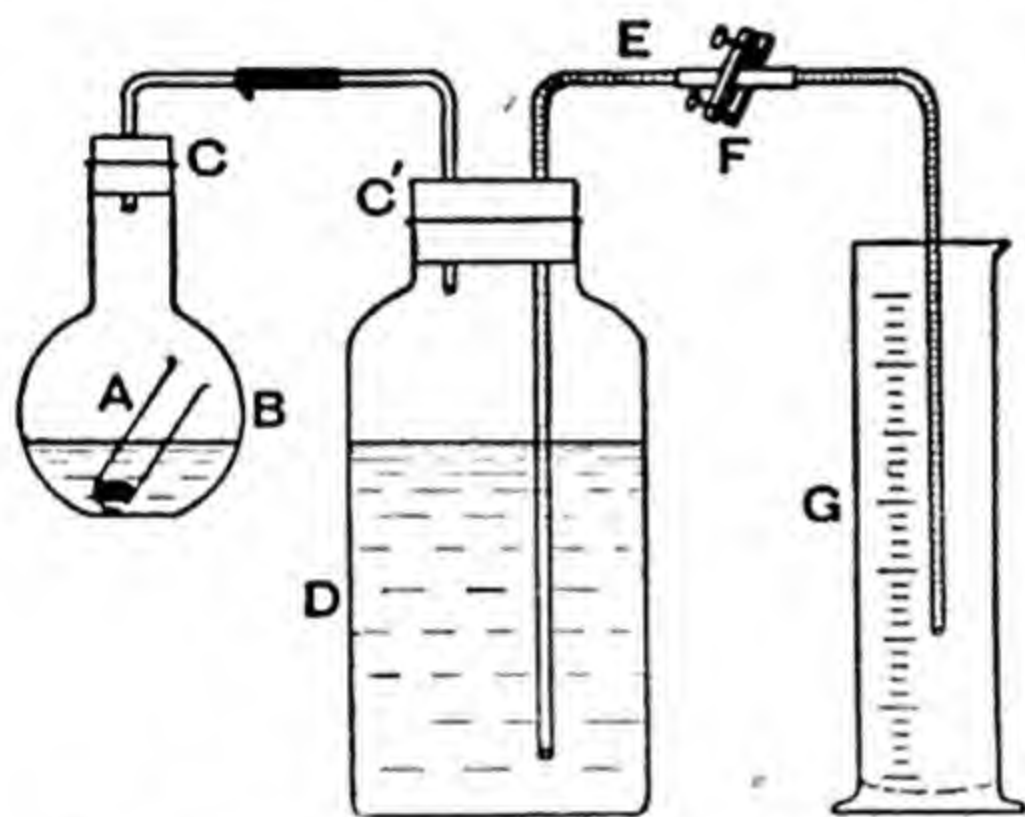


FIG. 109.—APPARATUS FOR DETERMINING THE EQUIVALENT OF A METAL WHICH DISSOLVES IN ACID (OR ALKALI) WITH EVOLUTION OF HYDROGEN.

metal does not come in contact with the liquid. The flask is firmly fixed to the rubber stopper *C* communicating by a bent tube passing through another rubber stopper *C'* with a large bottle *D* containing about a litre of water. The screw clip *F* on the rubber connection of the tube *E* is now opened and water allowed to run out so as to equalise the pressures. An empty graduated cylinder *G* is now placed under the end of the tube *E*, as shown, and the metal in *A* brought into the liquid in *B* by shaking. The metal is allowed to dissolve completely, heat being applied to the flask *B* if necessary. When the action is finished the whole is allowed to cool; the delivery tube should reach nearly to the bottom of the cylinder *G*, so that only water is drawn back into *D* on cooling. The water levels in *D* and *G* are equalised, the clip *F* is firmly closed, and the cylinder *G* removed. The volume of water in *G* is read off: this is equal to the volume of gas evolved. The temperature of the water is found by a thermometer and the barometric pressure read.

It is now possible to calculate the number of c.c. of hydrogen, measured at *S.T.P.*, evolved by 1 gram of metal. One c.c. of hydrogen at *S.T.P.* weighs 0.00009 gram, hence we can easily



calculate the weight of this hydrogen. To find the equivalent of the metal we now calculate what weight of metal liberates 1 gram of hydrogen.

*Example.*—1.68 gm. of zinc when dissolved in dilute sulphuric acid in the apparatus described liberated 606 c.c. of hydrogen, measured at 748 mm. pressure and at 11° C. The volume of hydrogen at S.T.P. will be

$$606 \times \frac{748}{760} \times \frac{273}{284} = 573 \text{ c.c.}$$

The weight of this hydrogen is  $573 \times 0.00009 = 0.0517$  gm., therefore the weight of zinc which displaces 1 gm. of hydrogen

$$= \frac{1.68}{0.0517} = 32.5,$$

which, by definition, is the equivalent of zinc.

*Method 2.*—A metal which displaces another metal from a solution of a salt of the latter. Zinc and iron both displace copper from a solution of copper sulphate, and zinc displaces lead from a solution of lead acetate. About 1 gram of thin sheet zinc, for example, is weighed out and placed in a solution of copper sulphate. A red spongy deposit of copper is produced. When all the zinc has disappeared, the copper is filtered off on a weighed filter paper, washed, and dried in a steam oven. The paper and copper are weighed and the weight of copper found. The equivalent of zinc has been found by method 1; it is 32.5, hence the equivalent of copper is the weight displaced by 32.5 grams of zinc.

*Method 3.*—A metal which readily forms an oxide. In the case of magnesium, a weighed amount of clean magnesium ribbon is heated in a weighed porcelain crucible, at first with the lid loosely fitted until active combustion ceases, then with the lid off. The crucible is cooled and reweighed. The amount of magnesium combining with 8 parts of oxygen is the equivalent.

In the case of tin, a weighed amount of the metal is treated carefully in a weighed porcelain dish with concentrated nitric acid until violent action ceases and red fumes are no longer evolved. The residue is carefully heated on a sand bath until dry and then ignited over a Bunsen flame. The weight of oxide of tin formed is thus found, and the equivalent of tin is the weight of metal combining with 8 parts of oxygen. The same method may be used with copper, the copper nitrate being strongly heated to decompose it to copper oxide.

*Method 4.*—If a compound of an element with chlorine is dissolved in water and the solution mixed with a solution of silver nitrate, double decomposition occurs and a precipitate of silver chloride is formed. If this is filtered, dried, and weighed, the amount of chlorine in the original compound can be calculated, since it is known that 108 gm. of silver combines with 35.5 gm. of chlorine to form silver chloride. Thus the weight of the element combined with 35.5 parts of chlorine can be calculated, and this will be the equivalent.

It was found that 14.43 gm. of potassium chloride, when treated with silver nitrate, gave 27.73 gm. of silver chloride. The weight of chlorine corresponding with this is

$$27.73 \times \frac{35.5}{(108 + 35.5)} = 6.86 \text{ gm.},$$

hence, the 14.43 gm. of potassium chloride contained 6.86 gm. of chlorine combined with  $14.43 - 6.86 = 7.57$  gm. of potassium. The weight of potassium combined with 35.5 gm. of chlorine is therefore

$$7.57 \times \frac{35.5}{6.86} = 39 \text{ gm.}$$

and this is the equivalent of potassium.



## CHAPTER IX

### THE ATOMIC THEORY

**\*Atoms.**—The laws of chemical combination were first explained on the basis of the **atomic theory** by John Dalton. The atomic theory is an assumption regarding the structure of matter, which it supposes to be composed of very small indivisible particles, called **atoms**, from a Greek word meaning 'something which cannot be cut.'

The Greek philosophers were divided in their opinions as to the ultimate structure of matter; one school regarded it as filling space continuously, like a jelly, whilst the other school, beginning with Leukippos and Demokritos, about 500 B.C., considered that matter filled space discontinuously, like apples in a barrel, and that the smallest parts of matter were indivisible **atoms**. Asklepiades of Prusa, about 100 B.C., introduced the idea of small clusters of atoms, corresponding with what we call **molecules**.

Our information about the atomic theory of the Greeks is largely derived from Aristotle's criticism of it, and from the account of the version of it by Epicurus (300 B.C.) given in the long poem, *De Rerum Natura* ('of the nature of things') by the Roman, Lucretius (c. 57 B.C.).

Aristotle (384-322 B.C.) says: 'Leukippos thought he had a theory which was in harmony with sense, "for," said he, "that which is strictly speaking real is an absolute *plenum*; but the *plenum* is not one [undivided whole]. On the contrary, there are an infinite number of them, and they are invisible owing to the smallness of their bulk. They move in the void (for there is a void); and by their coming together they effect coming into being; by their separation, passing away.'"

Lucretius (in the translation of Thos. Creech, 1714), who calls the atoms 'seeds,' says:

'But solid seeds exist, which fill their place;  
And make a difference betwixt full and space.'

These, as I prov'd before, no active flame,  
 No subtle cold can pierce, and break their frame,  
 Tho' ev'ry compound yields : no pow'rful blow,  
 No subtle wedge divide, or break in two.  
 For nothing can be struck, no part destroy'd  
 By pow'rful blows, or cleft without a void,  
 And things that hold most void, when strokes do press,  
 Or subtle wedges enter, yield with ease.  
 If seeds then solid are, they must endure  
 Eternally, from force, from stroke secure.'

The theory was entirely qualitative, and although it was never lost sight of, it did not prove fruitful in chemistry until John Dalton (1766-1844) endowed the atoms of the chemical elements with fixed and different weights, representing their combining proportions.

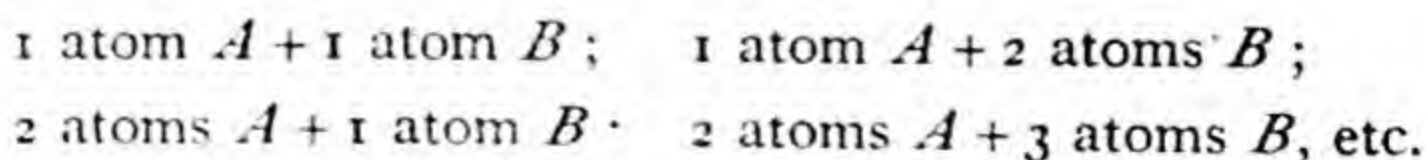
John Dalton was born at Eaglesfield, a village near Cocker-mouth in Cumberland, the son of Quaker parents. In 1781 he joined his brother in teaching in a school at Kendal, where he met John Gough, who stimulated his interest in mathematics and science. In 1793 he was appointed teacher of mathematics and natural philosophy in New College in Manchester, in which city he lived for the rest of his life, supporting himself by private tuition when New College moved to York. His note-books, found in the archives of the Manchester Literary and Philosophical Society in 1895 by Roscoe and Harden, show that Dalton was led, about 1803, to the atomic theory by speculations on mixtures of gases, under the influence of Newton, and afterwards extended it to explain the laws of chemical combination.

**Dalton's Atomic Theory.**—The chemical atomic theory asserts that :

(1) The **chemical** elements are composed of very minute particles of matter called atoms, which remain undivided in all chemical changes.

(2) Each kind of atom has a definite *weight*. Different elements have atoms differing in weight.

(3) Chemical combination occurs by the union of the atoms of the elements in simple numerical ratios, *e.g.*





These simple assumptions will explain the laws of chemical combination.

In the first place, atoms are indestructible in chemical changes, so that we see the necessity of the *law of indestructibility of matter* (p. 49). Secondly, the molecules of a compound are



FIG. 110.—JOHN DALTON, 1766-1844.

all alike, being formed of numbers of atoms of the two or more elements which do not vary from molecule to molecule; this explains the *law of constant proportions*. Thirdly, if elements combine in more than one proportion, the molecule of one compound must always differ from the molecule of the other compound by a whole number of atoms of one (or more) elements, which explains the *law of multiple proportions*. Lastly,

compounds of the elements  $A$  and  $C$  must be formed according to the scheme:  $m$  atoms  $A + n$  atoms  $C$ . Compounds of the elements  $B$  and  $C$  must be composed of:  $x$  atoms  $B + y$  atoms  $C$ . Compounds of the elements  $A$  and  $B$  must contain:  $p$  atoms  $A + q$  atoms  $B$ . But  $x, y, m, n, p, q$  are whole numbers, usually small. Hence  $p, q$  are either the same as  $m, x$ , or whole multiples of them, usually small. This is the *Law of Equivalent Proportions*.

The absolute weights of atoms, as Dalton realised, are very small indeed, and he therefore directed his attention to the determination of the relative weights, taking the weight of the lightest atom, that of hydrogen, as unity. If the absolute weight (or mass) of any *one* atom can be determined, those of all the others are found by simple multiplication of this by the ratios of the atomic weights. In recent years the mass of the hydrogen atom has been found by experiment to be  $1.66 \times 10^{-24}$  gm. Thus, 1 c.c. of hydrogen, at S.T.P., weighing 0.00009 gm., contains  $5.4 \times 10^{19}$  atoms.

Atomic weights are now referred to the weight of the *oxygen atom* as standard. This is taken as 16 units, so that if the weight of an atom of an element and the weight of an atom of oxygen are in the ratio  $A : 16$ , then  $A$  is the atomic weight of the element. On this scale the atomic weight of hydrogen is 1.008, but for elementary purposes this may be taken as 1. The equivalent of an element (p. 128) is, strictly, the weight combining with or displacing 8 parts by weight of oxygen.

The equivalent of an element will, from the definition, be either the atomic weight itself, or related to it in a simple manner, *i.e.*, it will be a simple fraction of it,  $\frac{1}{2}, \frac{1}{3}, \frac{2}{3}, \frac{2}{5}$ , etc., since 1 atom of the element combines with 1, 2, 3, etc., atoms of hydrogen, or two atoms of the element with 5, etc., atoms of hydrogen, and so on.

In its original form, Dalton's atomic theory provided no means of determining even the relative weights of the atoms. Although 8 parts of oxygen combine with 1 part of hydrogen, we do not know how many atoms of each element the molecule of the resulting water contains. If it contains 1 atom of each element (as Dalton supposed), the atomic weight of oxygen is 8, but if it contains 2 atoms of hydrogen to 1 atom of oxygen, as the volume ratio would suggest, the atomic weight of oxygen is  $2 \times 8 = 16$ .

The existence of *isotopes* (p. 126) shows that Dalton's assumption that the atoms of a given element are all alike is not correct





simpler and more easily remembered than it was until about the beginning of the nineteenth century, when a new system of chemical **nomenclature** (naming of substances) was introduced by Lavoisier and, shortly afterwards, a new system of **notation** (representing names by symbols) by Berzelius.

Let us first, in order to make this clear, look at the list of symbols in Fig. 111, which are taken from the early Greek chemical MSS. mentioned on p. 66. We notice that some are merely contractions of the Greek names for the materials (*e.g.*, vinegar,






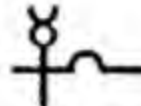









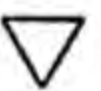
	Antimony		Mercury
	Arsenic		Salammoniac
	Vinegar		Corrosive sublimate
	Spirit of wine		Saltpetre
	Borax		Alkali
	Calx		Vitriol
	Realgar		Fire
	Soap		Water

FIG. 112.—ALCHEMIST'S SYMBOLS; FROM OSWALD CROLL'S *Basilica Chymica*, 1609.

crucible, juice, salt, arsenic); others, the symbols of the metals, are the symbols of the planets: Sun = gold; Moon = silver; Saturn = lead; Mars = iron; Venus = copper. This association of metals with planets came originally from Babylonia, as we know from cuneiform accounts and also from later Greek writers such as Proclus. The alchemists also made much use of the idea, and in their books we must understand by *sol* (= Sun) gold, and so on. We still use the name *mercury* for the metal (after the planet) and speak of silver nitrate as *lunar caustic*. Some of the other symbols have obvious derivations, but there are some of which we do not yet know the meanings.

The next list, in Fig. 112, from a textbook published in 1609, is similar. Some of the symbols are obvious modifications of



those in the first list (*e.g.*, arsenic), but there are several new symbols, *e.g.*, for antimony, spirit of wine, borax, and soap (the shape of which is that of a flake of 'Lux'). The symbol for corrosive sublimate is made up of the symbols for 'mercury' and 'vapour.'

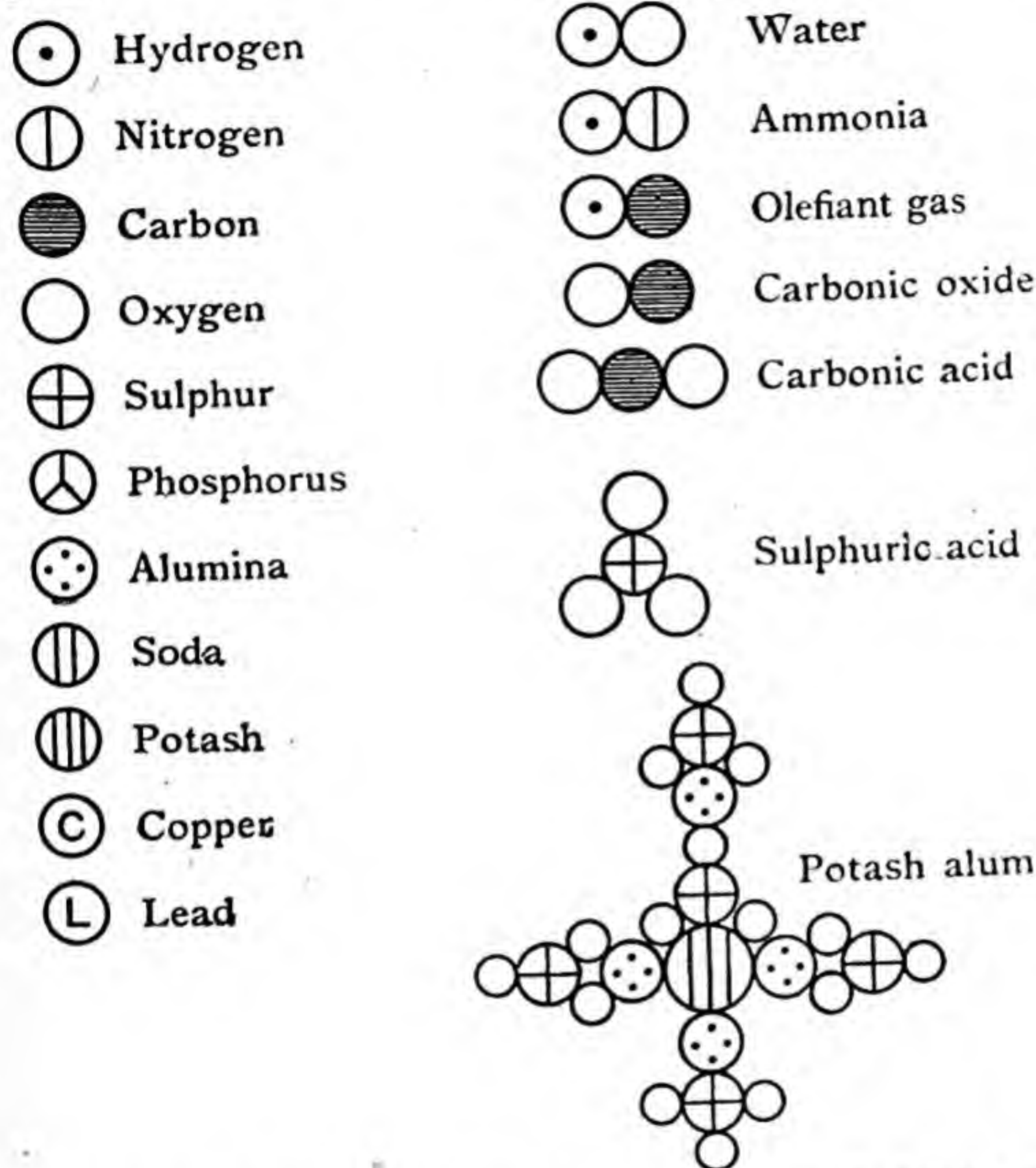


FIG. 113.—DALTON'S SYMBOLS AND FORMULAE FROM HIS *New System of Chemical Philosophy*, VOL. 1, 1808; VOL. 2, 1810.

The early chemical names were purely empirical, and a name frequently had one meaning to the adept and quite another to the ordinary man. The same substance had a variety of names, depending on its mode of preparation. Names were often based on accidental resemblances. Thus *butter of antimony* was classed along with ordinary butter, and *oil of vitriol* (sulphuric

acid) with olive oil. Such names as *liver of sulphur* (impure potassium sulphide) and *cream of tartar* (potassium hydrogen tartrate) arose in this way. Salts were often named after their discoverers, or the places where they were found (Glauber's salt, Epsom salt).

The symbols introduced by Dalton were, as we see from the few specimens reproduced in Fig. 113, not much better than the old ones, since there was no help to the memory in them. There was, however, one important step in advance, viz. that (besides the fact that each symbol represented one atom) the formula of a compound was made up of the symbols of its elements and also showed how many atoms of these were present in the molecule.

Berzelius's system of symbols is very simple. Every element is denoted by the *initial letter* (sometimes with another letter) *of the Latinised name of the element*, and in writing the formula of a compound, the symbols of its constituent elements are written down side by side, with a small whole number *below* each symbol to show how many atoms of it are present (the figure 1 being always understood). In French books these figures are sometimes written *above* the symbol.

The symbol of an element has a quantitative significance and represents one atom, or one atomic weight, of the element. Thus, H represents 1 part by weight of hydrogen; O represents 16 parts by weight of oxygen; Cl represents 35.5 parts by weight of chlorine, and so on. This is the most important feature of the system of chemical notation.

The symbols of the elements, with their atomic weights, are given in the table inside the front cover. The following are the less obvious symbols, which the reader should remember:

ENGLISH NAME.	LATIN NAME.	SYMBOL.
Antimony	<i>stibium</i>	Sb
copper	<i>cuprum</i>	Cu
mercury	<i>hydrargyrum</i>	Hg
silver	<i>argentum</i>	Ag
gold	<i>aurum</i>	Au
iron	<i>ferrum</i>	Fe
lead	<i>plumbum</i>	Pb
potassium	<i>kalium</i>	K
sodium	<i>natrium</i>	Na
tin	<i>stannum</i>	Sn

The symbol W given to tungsten is from the German name *wolfram*.



**The names of compounds.**—The names of compounds are formed from those of their constituents in such a way as to indicate their composition.

In the names of compounds of two elements, or **binary compounds**, the name of one element, the more electropositive



FIG. 114.—JOHN JACOB BERZELIUS, 1779-1848.

(p. 211), comes first, followed by the name of the other element, suitably contracted and with the termination *-ide* :

$\text{H}_2\text{S}$  hydrogen sulphide.  
 $\text{NaCl}$  sodium chloride.

$\text{Cl}_2\text{O}$  chlorine monoxide.  
 $\text{Mg}_3\text{N}_2$  magnesium nitride.

Since two elements often combine in more than one proportion, giving different compounds, this is represented in the nomenclature in one of two ways : (1) by suffixes, (2) by prefixes.

Thus, the two oxides of copper are :

Red oxide of copper,  $\text{Cu}_2\text{O}$ , cuprous oxide } Suffixes.  
 Black oxide of copper,  $\text{CuO}$ , cupric oxide }

Two oxides of sulphur are :

$\text{SO}_2$ , sulphur dioxide } Prefixes.  
 $\text{SO}_3$ , sulphur trioxide }

The suffix *-ous* denotes the *lower*, the suffix *-ic* the *higher*, proportion of an element. The suffixes are always added to the Latin names :

Green chloride of iron,  $\text{FeCl}_2$ , ferrous chloride, or iron dichloride.

Red chloride of iron,  $\text{FeCl}_3$ , ferric chloride, or iron trichloride.

In a series of oxides, the one containing most oxygen is often (but not always) called the *peroxide*.

**Chemical equations.**—A chemical change occurring between substances, or a **chemical reaction**, may be represented by a **chemical equation**. In this we write down the formulae of the substances which react, and those of the substances formed by the reaction. The formulae of the interacting substances are connected by plus (+) signs, as are those of the products of reaction, and the set of initial substances is separated from the set of products by the sign equals (=). Each symbol represents a definite weight of the substance, as explained, and since the total weight of any element must be the same after as before the reaction, the equation must express this by containing the same number of atoms of *each* element on both sides of the equals sign. The equation is then said to be *balanced*, and an equation is never correct unless it is so balanced. For example, the combination of hydrogen and oxygen to form water is not correctly represented by the equation:  $\text{H} + \text{O} = \text{H}_2\text{O}$ , but the equation  $2\text{H} + \text{O} = \text{H}_2\text{O}$  represents the correct number of atoms on each side, is a balanced equation, and is so far correct.

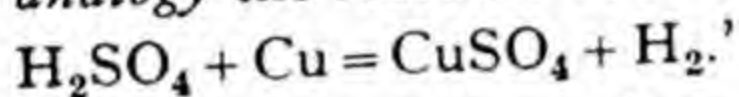
The student should avoid forming the careless habit of leaving equations unbalanced with the sign  $\rightarrow$  instead of =.

Although an equation can never be correct unless it is balanced, it is by no means necessary that a balanced equation is a correct representation of facts. For instance, we shall soon see that the correct way of representing hydrogen and oxygen *gases* is by the symbols  $\text{H}_2$  and  $\text{O}_2$ , and therefore that the correct equation is not  $2\text{H} + \text{O} = \text{H}_2\text{O}$  but  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ . Again, in order that a correct equation may be written, we must know



that *the change it represents can really take place*, and that the products are really those which are shown in the equation.

Although the equation  $C + 2Cl_2 = CCl_4$  is balanced, and although chloride of carbon is correctly represented by the formula  $CCl_4$ , this equation is nevertheless incorrect, because carbon chloride cannot be produced by the action of carbon on chlorine. We cannot invent methods of preparing substances in this way, and chemical equations must always be based on facts. Again, we might attempt to answer the question, 'What is the action of sulphuric acid on copper?' by a process of reasoning as follows: 'The action of sulphuric acid on zinc is to give zinc sulphate and hydrogen, and the equation for the reaction is  $H_2SO_4 + Zn = ZnSO_4 + H_2$ . Copper sulphate is  $CuSO_4$ , and it will probably be formed from sulphuric acid and copper, so that *by analogy* the reaction will be



This will, however, be quite wrong, since, although copper sulphate is formed, hydrogen is not, and the correct equation is  $2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2$ . Reasoning by analogy is especially unsafe and unreliable in chemistry, and unless the student *knows* how a reaction takes place he will nearly always be wrong if he attempts to *represent* the reaction by an equation made up by analogy with some other reaction.

**Acids, bases, and salts.**—Compounds of *three* elements are called **ternary compounds**; the most important belong to the classes known as **acids, bases, and salts**, containing oxygen. The terminations **-ous** and **-ic** are then used to distinguish *acids* containing less and more oxygen, the terminations **-ite** and **-ate** being used for the corresponding *salts*:

ACID.	SALT.
Sulphurous, $H_2SO_3$ .	Sodium sulphite, $Na_2SO_3$ .
Sulphuric, $H_2SO_4$ .	Cupric sulphate, $CuSO_4$ .
Nitrous, $HNO_2$ .	Potassium nitrite, $KNO_2$ .
Nitric, $HNO_3$ .	Lead nitrate, $Pb(NO_3)_2$ .

Oxides yielding acids with water are called **acidic oxides**, or **acid anhydrides** (*a without*; ὑδωρ (*hudor*) *water*):

$SO_2$ , sulphurous anhydride.	$SO_3$ , sulphuric anhydride.
$P_2O_3$ , phosphorous anhydride.	$P_2O_5$ , phosphoric anhydride.
$N_2O_3$ , nitrous anhydride.	$N_2O_5$ , nitric anhydride.

By the combination of acidic oxides with water, **acids** are produced:  $SO_3 + H_2O = H_2SO_4$  (sulphuric acid).

Oxides reacting with acids to form salts are called **basic oxides**.

By the combination of some basic oxides with water, bases are produced. These contain a metal (or radical, *cf.* below) united with a group of atoms OH, called **hydroxyl**, and they are therefore called **hydroxides** (not 'hydrates'; p. 39). Hydroxides of sodium, potassium, and other so-called alkali-metals are called **alkalies**; oxides of calcium, strontium, and barium are called **alkaline earths**.

$K_2O + H_2O = 2KOH$  (potassium hydroxide, caustic potash).

$CaO + H_2O = Ca(OH)_2$  (calcium hydroxide, slaked lime).

Acidic and basic oxides *combine* to form salts:

$SO_3 + Na_2O = Na_2SO_4$  (sodium sulphate).

Acids and bases react to produce salts, but water is formed at the same time:

$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$ .

The salt  $Na_2SO_4$  may be regarded as sulphuric acid in which two atoms of hydrogen are replaced by two atoms of sodium. Thus, acids may be considered as **salts of hydrogen**, which hydrogen can be displaced by metals. This takes place directly, for instance, when metallic zinc dissolves in dilute sulphuric acid:

$Zn + H_2SO_4 = ZnSO_4$  (zinc sulphate) +  $H_2$ .

Salts are also formed by the action of acids on basic oxides, or carbonates; in the second reaction (below), gaseous carbon dioxide is evolved with effervescence:

$CuO + H_2SO_4 = CuSO_4 + H_2O$

$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ .

**Radicals.**—In certain compounds a *group of atoms* plays the part of a single atom, and occurs in a whole series of combinations with other atoms. Thus the salts formed by the combination of ammonia,  $NH_3$ , with acids all contain the group  $NH_4$ , which plays the part of a metal, and is called **ammonium**:

$NH_3 + HCl = NH_4Cl$ , ammonium chloride (*cf.* potassium chloride,  $KCl$ ).

$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$ , ammonium sulphate (*cf.* potassium sulphate,  $K_2SO_4$ ).

Such an unvarying group of atoms present in a series of closely related compounds is called a **radical** (Latin, *radix*, a root). The group OH (hydroxyl) in bases is a radical.



**General properties of acids and bases.**—Although typical representatives of acids, bases, and salts, three important classes of chemical compounds, have been mentioned, no attempt has been made to give logical definitions of the groups—a matter of some difficulty, since the properties of one can hardly be specified without reference to those of the other two members.

The ancients knew only one acid, viz. common *vinegar*, or crude *acetic acid*, produced by the oxidation of wine, which becomes sour on exposure to air (Greek *oxos*, vinegar; *oxus*, sour). They knew that vinegar effervesced with natural sodium carbonate (*nitrum*, Proverbs xxv, 20), and the solvent properties of acids figure in the story of Cleopatra and the pearl. Other acids (sulphuric, nitric, hydrochloric) were discovered by the alchemists; Scheele (1770-1786) isolated a number of *organic acids*, i.e., acids containing carbon, hydrogen, and oxygen, of which acetic acid is an example. These acids, such as citric, tartaric, and malic, impart a sour taste to unripe fruits, whilst the acidity of sour milk is due to lactic acid.

Boyle (1663) recognised the following as the properties of acids :

- (1) They possess a sour taste.
- (2) They act as solvents, but with varying power on different bodies; the varying *strengths of acids* was recognised by Tachenius in 1666.
- (3) They precipitate sulphur from a solution of liver of sulphur (polysulphides of potassium).
- (4) They turn many blue vegetable colours (e.g., litmus) red, the colour being restored by alkalies.
- (5) They react with alkalies, the characteristic properties of each substance disappearing, and a *neutral salt* being formed.
- (6) Cavendish (1766) showed that hydrogen is evolved by the action of acids (except nitric) on zinc, iron, and tin.

Examples of *alkaline substances*, such as wood ashes, and *natron* (native sodium carbonate) were known to the ancients. The alchemists of the thirteenth century were acquainted with ammonium carbonate in the form of *spirit of hartshorn*, prepared by the destructive distillation of horn and bones, or the putrefaction of urine (cf. p. 378). Later on, it was found that the salt obtained by the lixiviation (extraction with water: Latin *lix*, ashes) of the ashes of plants growing on the sea littoral had the same properties as natron, whilst seaweeds contained the same alkali as wood ashes. The Iatrochemists first described the general properties of alkalies. These properties

were found to be enhanced by boiling with milk of lime, and the names **mild alkali** and **caustic alkali** were introduced for the alkali before, and after, this treatment, respectively. The difference between mild and caustic alkalies was explained by Black in 1754, as we shall see later.

As **general properties of alkalies**, the following were recognised :

(1) Their solutions feel soapy when rubbed between the fingers. (This is probably due to corrosion of the skin, since it is felt with concentrated sulphuric acid ; acids when diluted usually feel very harsh when so treated.)

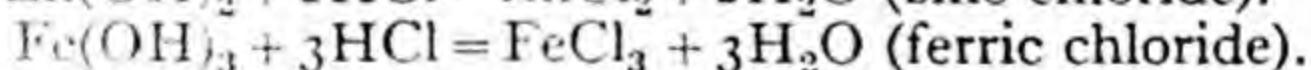
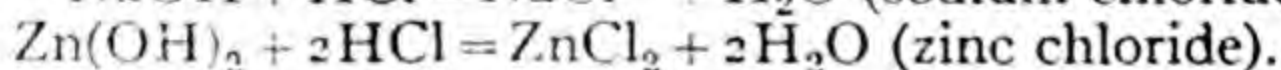
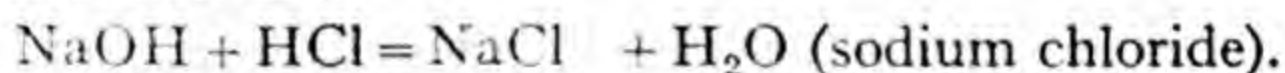
(2) They restore the blue colour of dyes reddened by acids (*e.g.*, red cabbage, litmus), and turn the extract of violets green.

(3) They neutralise acids to form salts.

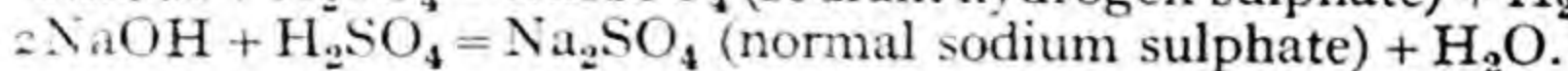
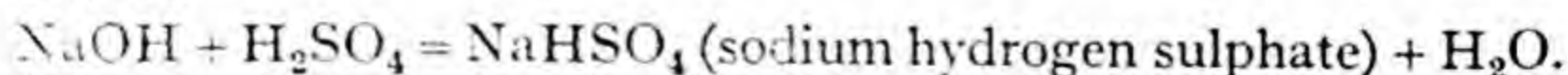
(4) The 'mild' varieties effervesce with acids, giving off 'fixed air' (carbon dioxide).

**Normal, acid and basic salts.**—By the interaction of acids and bases, **salts** are produced, together with water. Salts are named after the commonest representative of the class, viz. common salt. It is not possible to give a table of general properties of salts. For instance, they have not all a 'salty' taste : some are nearly tasteless, some are sweet, others have a 'metallic' taste, etc. Again, some salts are soluble, others are insoluble, and so on. The classes of salts called **normal**, **acid**, and **basic** salts may be defined at the present stage.

When an acid contains in the molecule only *one* atom of hydrogen which can be replaced by a metal, it can form only one class of salts. Thus, hydrochloric acid can give chlorides in which *all* the hydrogen has been replaced by a metal. It is called a **monobasic acid** :



When an acid contains in the molecule *two* atoms of hydrogen which can be replaced by metals, it can form *two* classes of salts. Either both atoms of hydrogen are replaced, forming a **normal** salt, or only one, when an **acid salt** is formed. Sulphuric acid is dibasic.



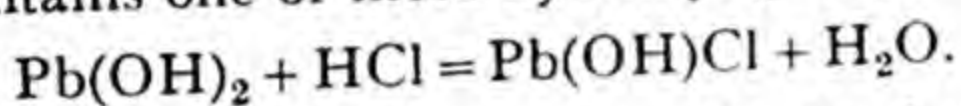
It must be remembered that an acid salt is not necessarily acid to litmus : acid sodium carbonate,  $\text{NaHCO}_3$ , derived



from carbonic acid,  $\text{H}_2\text{CO}_3$ , is alkaline to litmus. The name 'normal' is practically never used in speaking of salts individually: we say simply 'sodium sulphate,' etc. Sometimes acid salts, besides being called sodium *hydrogen* sulphate, sodium *hydrogen* carbonate, etc., are called *bisulphate*, *bicarbonate*, etc.

We can see the reason for this from the old formulae of these salts:  $\text{Na}_2\text{O} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ , etc., in which they are represented as made up of acid and basic oxides.

Basic salts may be regarded from two points of view. We have seen that all bases contain *hydroxyl*,  $\text{OH}$ , which interacts with the acidic hydrogen of acids to form water, and the other atom or radical of the base then forms a salt with the radical of the acid. When, however, a base contains more than one hydroxyl group, we may suppose that a salt can be formed which still contains one or more hydroxyl groups of the base:



We call  $\text{Pb}(\text{OH})\text{Cl}$  *basic lead chloride*. It is found, however, that basic salts very rarely have such simple formulae as this would suggest, and it is usual to regard them as compounds of normal salts with free base or basic oxide. Thus, the common basic lead chloride is  $\text{PbCl}_2, 7\text{PbO}$ , and basic copper carbonate is  $\text{CuCO}_3, \text{Cu}(\text{OH})_2$ . Some so-called basic salts may be merely mixtures of normal salts with basic oxide or hydroxide.

**Chemical calculations.**—The systematic notation of chemistry leads to a great simplification of numerical calculations. *The symbol of an element represents one atom, i.e., a definite weight, and the formula of a compound represents one molecule, the weight of which is the sum of the weights of the atoms contained in it.* The unit of weight is quite arbitrary. For example,  $\text{O}$  means 16 grams, ounces, pounds, etc., of oxygen;  $\text{CuO}$  means 79 grams, ounces, pounds, etc., of cupric oxide.

The interaction of elements and compounds is shown by **chemical equations**. Since the symbols denote atomic and molecular weights, the same number of atoms of the same elements must occur (in different groupings, it is true) on each side of a chemical equation; or, as is said, *the equation must balance*.

The formula of a compound is easily found from its percentage composition, and *vice versa*. The simplest possible formula derived from the percentage composition is called the **empirical formula**.

To find the formula from the percentage composition, divide the percentage of each element by its atomic weight and so obtain a series of numbers in the ratio of the numbers of atoms of the elements in the molecule of the compound. This series, reduced to the ratios of the smallest *whole* numbers, will give the empirical formula.

The slight differences from whole numbers often found are due to experimental errors in the percentage composition.

*Example 1.*—Potassium chlorate contains 31.84 per cent. of potassium, 28.98 per cent. of chlorine and 39.18 per cent. of oxygen. Find its empirical formula ( $K=39$ ;  $Cl=35.5$ ;  $O=16$ ).

The relative numbers of atoms of the elements in a molecule of potassium chlorate are :

POTASSIUM.	CHLORINE.	OXYGEN.
$\frac{31.84}{39} = 0.8162$	$\frac{28.98}{35.5} = 0.8162$	$\frac{39.18}{16} = 2.4486,$
<i>i.e.</i> $\frac{0.8162}{0.8162} = 1$	$\frac{0.8162}{0.8162} = 1$	$\frac{2.4486}{0.8162} = 3 ;$

$\therefore$  the formula is  $KClO_3$ .

*Example 2.*—Find the percentages of the elements in nitric acid,  $HNO_3$  :

$$HNO_3 = 1 + 14 + 3 \times 16 = 63$$

Thus, 63 parts by weight of nitric acid contains 1 part of hydrogen, 14 parts of nitrogen and 48 parts of oxygen. The weights of the elements in 100 parts by weight of nitric acid are the percentages required.  $\therefore$  Thus :

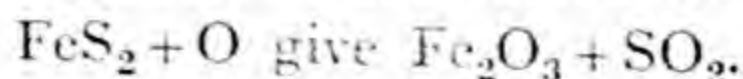
$$\text{percentage of hydrogen} = 1 \times \frac{100}{63} = 1.59$$

$$\text{percentage of nitrogen} = 14 \times \frac{100}{63} = 22.22$$

$$\text{percentage of oxygen} = 48 \times \frac{100}{63} = \frac{76.19}{100.00}$$

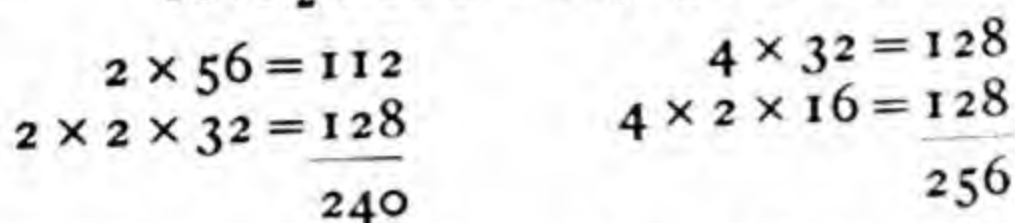
*Example 3.*—What weight of iron pyrites ( $FeS_2$ ) must be burnt in air to give 100 grams of sulphur dioxide ?

First write the equation in *unbalanced* form :





To form  $\text{Fe}_2\text{O}_3$  we shall require  $2\text{FeS}_2$ . The  $2\text{Fe}$  will require  $3\text{O}$  and the  $2\text{S}_2$ , *i.e.*,  $4\text{S}$  will require  $4 \times 2 = 8\text{O}$  to form  $\text{SO}_2$ . Hence, in all,  $8 + 3 = 11\text{O}$  will be required. The *balanced* equation is :

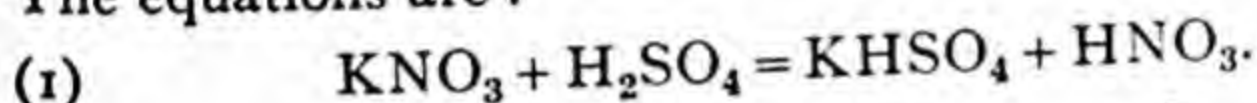


Therefore 240 grams of pyrites give 256 grams of  $\text{SO}_2$ , so that the weight required for 100 grams of  $\text{SO}_2$  will be :

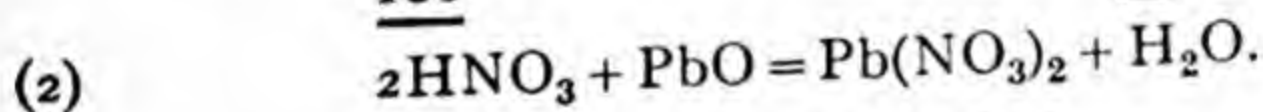
$$240 \times \frac{100}{256} = 93.76 \text{ grams.}$$

*Example 4.*—Five hundred grams of potassium nitrate are decomposed by sulphuric acid in a glass retort and the nitric acid produced neutralised with lead oxide. What is the greatest weight of lead nitrate which can be formed?

The equations are :



$39$	$1$
$14$	$14$
$3 \times 16 = 48$	$3 \times 16 = 48$
<u>101</u>	<u>63</u>



$2 \times 63$	$207$
$2 \times 14 = 28$	$28$
$3 \times 2 \times 16 = 96$	$96$
	<u>331</u>

We see that 101 grams of potassium nitrate give 63 grams of nitric acid, and that  $2 \times 63$  grams of nitric acid give 331 grams of lead nitrate. Hence, to form 331 grams of lead nitrate we must take  $2 \times 101 = 202$  grams of potassium nitrate. Therefore, from 500 grams of potassium nitrate we shall obtain :

$$\frac{500}{202} \times 331 = 819.3 \text{ grams of lead nitrate.}$$

(*N.B.*—The *separate* calculations for equations (1) and (2) are not required.)

## CHAPTER X

### MOLECULES

**Gay-Lussac's law of gaseous volumes.**—The relative combining volumes of hydrogen and oxygen were found by Cavendish



FIG. 115.—JOSEPH LOUIS GAY-LUSSAC, 1778-1850.

to be very nearly 2 : 1. Alexander von Humboldt and Joseph Louis Gay-Lussac in 1805 confirmed this result, and the latter,



impressed by the simplicity of the ratio, extended the researches to other chemical reactions between gases. In 1808 he deduced the following law: When chemical changes occur between gases, there is always a simple relation between the volumes of the interacting gases, and also of the products, if these are gaseous. The same conditions of temperature and pressure are assumed.

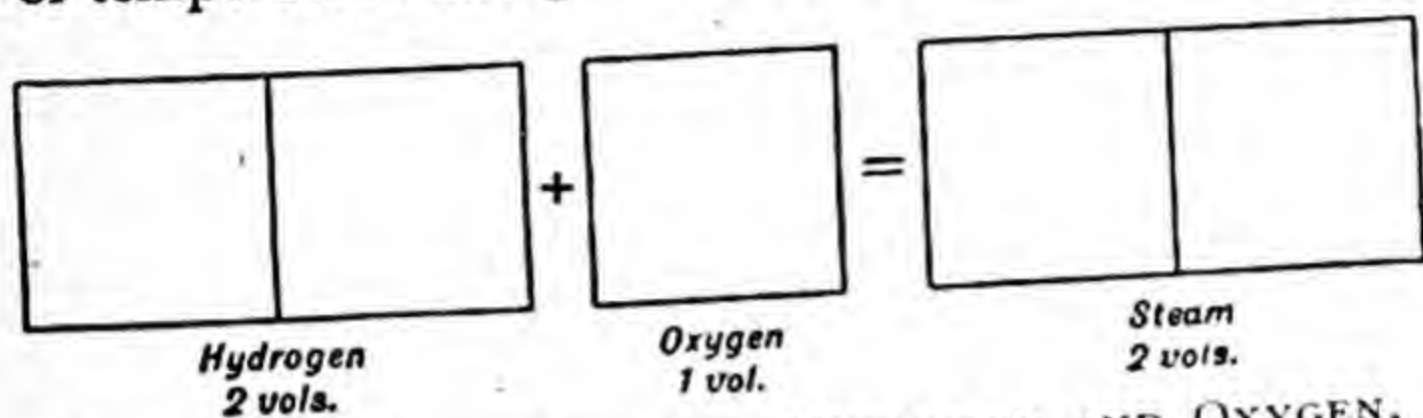


FIG. 116.—COMBINATION OF HYDROGEN AND OXYGEN.

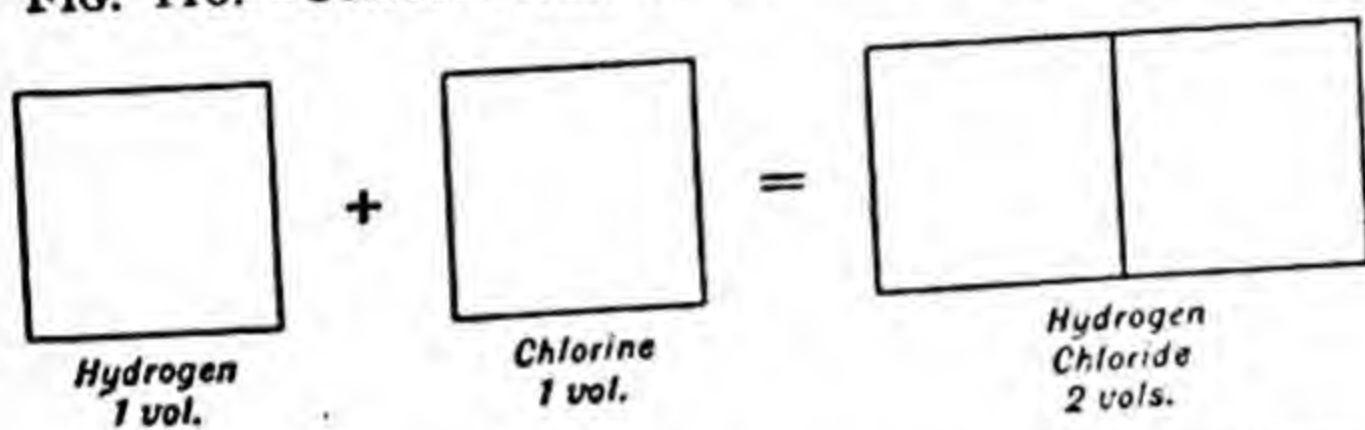


FIG. 117.—COMBINATION OF HYDROGEN AND CHLORINE.

Let us in the first place represent the volumes by squares, which we may regard as sections of cubes containing equal volumes of the gases.

Gay-Lussac remarked that, since gases combine *by weight* in atomic proportions, or simple multiples of these, and *by volume* in simple ratios, there must be some simple relation between the atomic weights and the combining volumes. Berzelius assumed that equal volumes of elementary gases contain equal numbers of atoms.

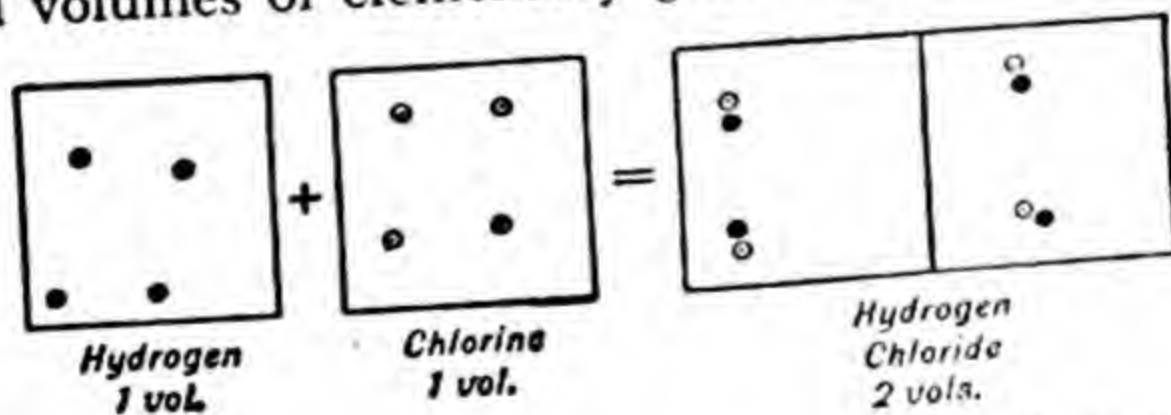


FIG. 118.—COMBINATION OF HYDROGEN AND CHLORINE.

Let us see how this works out if we assume that the compound gas also contains, in the same volume, the same number of

particles as the elementary gases. Take the case of hydrogen and chlorine and represent a hydrogen atom by  $\bullet$  and a chlorine atom by  $\odot$ .

We see that we cannot make the volumes right, because to do this, hydrogen chloride would have to contain only half as many particles as an equal volume of hydrogen or chlorine. Dalton pointed out this difficulty. It was overcome in a surprisingly simple way by the Italian physicist, Avogadro, in 1811.



FIG. 119.—AMEDEO AVOGADRO (1776-1856).

**Avogadro's hypothesis.**—Avogadro began by assuming that the simple hypothesis of equal numbers of particles (**molecules**) in equal volumes is correct. The discrepancies must then arise from an incorrect method of applying the hypothesis to the experimental results.

Avogadro's hypothesis states that **equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain identical numbers of molecules.** It shows that 'the ratios of the masses of the molecules are the same as those of the densities of the different gases at equal temperature and pressure.'



By a molecule is meant the smallest mass of a substance capable of independent existence.

Avogadro now showed that *the molecules of the elementary gases are not necessarily the atoms themselves, but usually consist of groups of atoms, behaving as though they were single particles*. The number of atoms in a molecule is sometimes called the **atomicity**: argon, A, is monatomic; oxygen,  $O_2$ , diatomic; ozone,  $O_3$ , triatomic; phosphorus,  $P_4$ , tetraatomic, etc.

Let us assume that the molecules of both hydrogen and chlorine contain *two* atoms each, and that they are divided when the gases react. Then the volume relations will come out correctly, as we see :

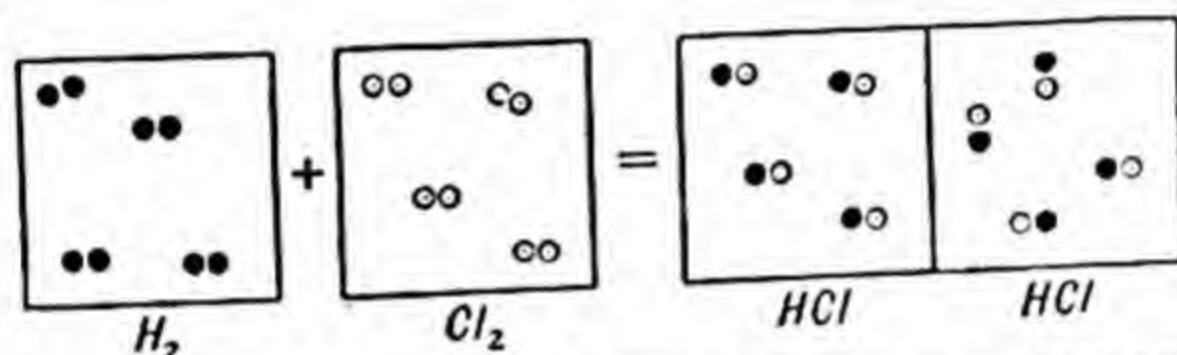
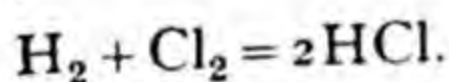


FIG. 120.—COMBINATION OF HYDROGEN AND CHLORINE.

or, in ordinary symbols :



Another example is the formation of steam from hydrogen and oxygen :

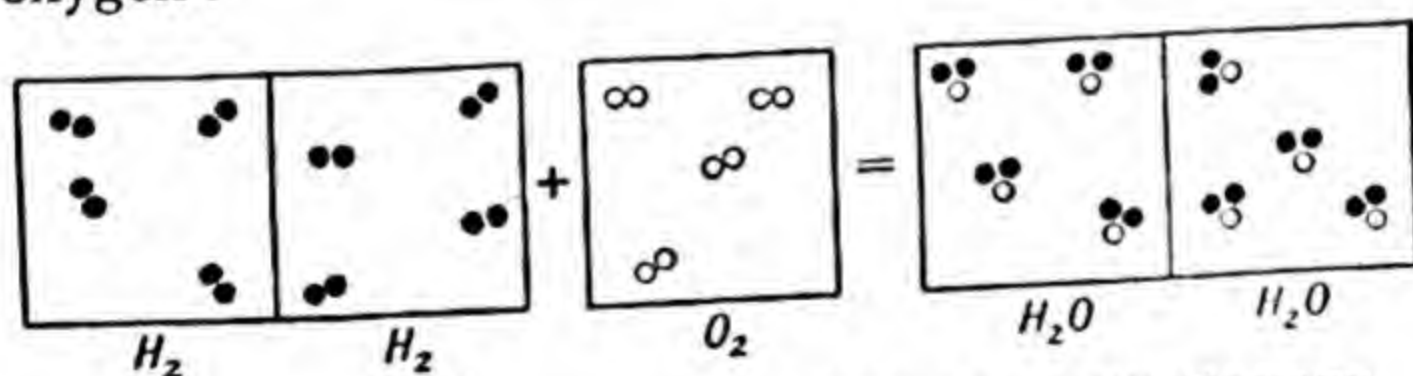


FIG. 121.—COMBINATION OF HYDROGEN AND OXYGEN.

Now consider the combustion of carbon in oxygen to form carbon dioxide. In this case we know nothing of the composition of the molecules of carbon, since these are present in a *solid*, to which Avogadro's hypothesis does not apply. If we *assume* that *one* atom of carbon combines with *two* atoms of oxygen to form a molecule of carbon dioxide, the fact that no change in volume occurs when carbon burns in oxygen is explained, but it is clear that the same result is obtained if we assume that

$n$  atoms of carbon combine with 2 atoms of oxygen to produce a molecule of carbon dioxide. The only result which may be deduced directly is that a molecule of carbon dioxide contains a molecule of oxygen (2 atoms).

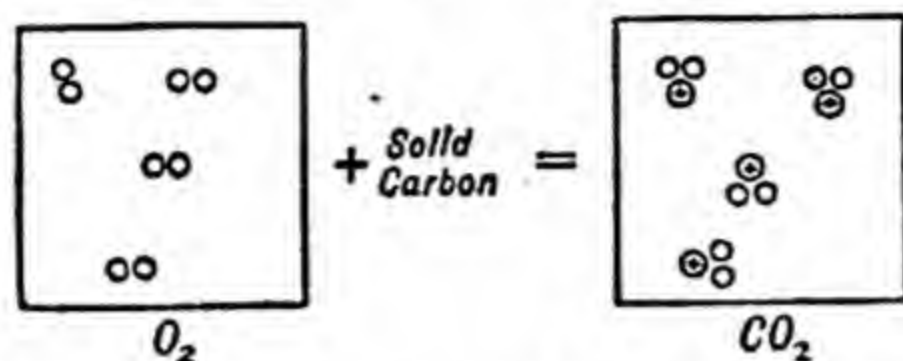


FIG. 122.—COMBUSTION OF CARBON IN OXYGEN.

**Molecular weight and vapour density.**—According to Avogadro's hypothesis, the weights of equal volumes of gases are proportional to the molecular weights. Since hydrogen is the lightest gas known, the molecular weights of other gases may be compared with that of hydrogen by finding the ratios of the weights of equal volumes of the gases to the weight of the same volume of hydrogen. These ratios are called the **vapour densities** (p. 121). If it is assumed that the molecular weight of hydrogen be 1, the vapour density would be equal to the molecular weight, but as it is known from what precedes that the hydrogen molecule contains *two* atoms, its molecular weight must be 2, and the molecular weight of any gas or vapour is therefore twice its vapour density. This result does not, of course, depend on how many atoms are contained in the molecule of the gas, but only on the assumption that there are two atoms in the molecule of *hydrogen*.

This reasoning may be set out in the following form :

$$\begin{aligned}
 \text{Vapour density} &= \frac{\text{Wt. of any vol. of gas or vapour}}{\text{Wt. of an equal vol. of hydrogen}} \\
 &= \frac{\text{Wt. of } n \text{ molecules of substance}}{\text{Wt. of } n \text{ molecules of hydrogen}} \\
 &= \frac{\text{Wt. of one molecule of substance}}{\text{Wt. of one molecule of hydrogen}} \\
 &= \frac{\text{Molecular wt. of substance}}{\text{Molecular wt. of hydrogen}};
 \end{aligned}$$

$\therefore$  Molecular wt. of substance = vapour density  $\times$  molecular wt. of hydrogen ;

$\therefore$  Molecular weight = vapour density  $\times$  2.



It may be noted that *the standard of molecular weight is the atom, not the molecule, of hydrogen*. This must be so if molecular weights of compounds are to be formed by adding together the weights of their component atoms.\*

**Determination of atomic weight from gas or vapour densities.**—The Italian chemist Cannizzaro, in 1858, showed that Avogadro's



FIG. 123.—STANISLAO CANNIZZARO, 1826-1910.

hypothesis can be applied in the determination of atomic weights. By means of vapour density measurements, the molecular weights of volatile compounds of an element are found. By analysis is then found what weights of the particular element

\* The standard of atomic weights now adopted is the atomic weight of oxygen taken as 16, which makes that of hydrogen 1.008. This gives a factor 2.016 instead of 2 in the above reasoning, which does not affect it in principle.

are contained in the molecular weights of all the various compounds. These must be whole multiples of the atomic weight, and, if the number of compounds taken is large enough, at least one of the weights of the element present in the molecular weights of its compounds will probably be the atomic weight itself.

The atomic weight of an element is the least weight of the element contained in a molecular weight of any of its compounds.

It will be seen that this is not an independent definition of atomic weight, but is merely a consequence of Avogadro's hypothesis.

It cannot be emphasised too strongly that the determination of the relative density of *one compound* of an element, or of *the element itself* if it is volatile, can give no sure indication of the atomic weight. The molecules of the particular compound selected, and those of the vapour of the free element, may contain one, two, three, or more atoms of the element, for all we know to the contrary. The larger the number of compounds investigated, the greater is the probability that at least one contains only one atom of the element in a molecule.

#### OXYGEN COMPOUNDS.

Compound.	Vap. density. (H=1) $\Delta$	Mol. wt. $= 2 \times \Delta$	Wt. of oxygen in one mol. wt. of compound.
Oxygen gas - -	16	32	$16 \times 2$
Water - - -	9	18	16
Carbon monoxide -	14	28	16
Carbon dioxide -	22	44	$16 \times 2$
Sulphur dioxide -	32	64	$16 \times 2$
Sulphur trioxide -	40	80	$16 \times 3$
Nitrous oxide -	22	44	16
Nitric oxide - -	15	30	16

The least weight of oxygen found in a molecular weight of any one of these compounds is 16, and hence this is taken as the atomic weight.

A molecule of water contains one atom of oxygen, of weight 16, and therefore contains  $18 - 16 = 2$  parts, or two atoms, of hydrogen. The formula of water is therefore  $H_2O$ . In this way the problem which had eluded Dalton, of finding the number of atoms of the elements in the molecule of a compound, is easily solved.

Similarly, a table of carbon compounds may be drawn up.



## CARBON COMPOUNDS.

Compound.	Vap. density. (H=1) $\Delta$	Mol. wt. $= 2 \times \Delta$	Wt. of carbon in one mol. wt. of compound.
Methane - - -	8	16	12
Ethane - - -	15	30	$12 \times 2$
Ethylene - - -	14	28	$12 \times 2$
Alcohol - - -	23	46	$12 \times 2$
Ether - - -	37	74	$12 \times 4$
Benzene - - -	39	78	$12 \times 6$
Carbon monoxide -	14	28	12
Carbon dioxide -	22	44	12

The atomic weight of carbon deduced from these results is 12. Thus, in 78 parts of benzene there are 72 parts, or 6 atoms, of carbon. Hence there are  $78 - 72 = 6$  parts, or 6 atoms, of hydrogen. The formula of benzene is thus  $C_6H_6$ .

The molecular weights found from the vapour densities are only approximate, since the determinations are usually made only roughly and the gases or vapours do not obey Boyle's and Charles's laws accurately, nor do equal volumes contain exactly equal numbers of molecules. The *accurate* values of the atomic and molecular weights are found from the refined chemical analyses of the compounds, and the vapour density measurements are used simply to decide between various possible *molecular* weights (see p. 183).

It is possible, by making very accurate measurements of the densities of *gases* and then making corrections based on the deviations from Boyle's law shown by each particular gas, to obtain very exact values for the molecular weights, and thence atomic weights.

**Gram-molecular volume.**—The molecular weight in grams of any substance is called the **gram-molecular weight**, or **mol** (pronounced *mole*): in the case of a gas this will occupy a fixed volume at S.T.P. which is called the **gram-molecular volume**, or **molar volume**.

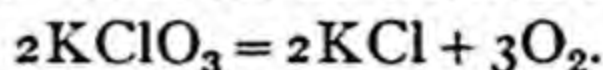
One litre of oxygen at S.T.P. weighs 1.429 grams, hence the volume of 32 grams of oxygen at S.T.P. is  $32/1.429 = 22.4$  litres, which is the molar volume. Avogadro's hypothesis shows that the molar volume of *any* gas at S.T.P. is 22.4 litres.

In calculations involving volumes of gases, the chemical equations must be written so as to express reactions between *molecules* of the gases, since only in this case are the volume relations correctly given.

Thus, the equation  $\text{H} + \text{Cl} = \text{HCl}$ , although it gives the correct *weight* ratios, does not give the correct *volume* ratio. This is expressed by the molecular equation:  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ .

*Example 1.*—Find the volume of oxygen, measured at  $15^\circ$  and 740 mm., evolved on heating 5 grams of potassium chlorate.

The equation  $\text{KClO}_3 = \text{KCl} + 3\text{O}$  does not show the production of oxygen molecules. It must be written:



$$\begin{array}{rcl} 2 \times 39 & = & 78 \\ 2 \times 35.5 & = & 71 \\ 2 \times 3 \times 16 & = & 96 \\ \hline & & 245 \end{array} \qquad \begin{array}{l} 3 \times 22.4 \text{ litres} \\ \text{at S.T.P.} \\ = \text{vol. of 3 mols at S.T.P.} \end{array}$$

Thus, 245 grams of chlorate give  $3 \times 22.4$  litres of oxygen at S.T.P. Five grams will give:

$$\frac{5}{245} \times 3 \times 22.4 \text{ litres at S.T.P.}$$

At a pressure of 740 mm. at  $0^\circ \text{C}$ . this will occupy

$$\frac{5}{245} \times 3 \times 22.4 \times \frac{760}{740} \text{ litres,}$$

and at the pressure of 740 mm. but at  $15^\circ \text{C}$ . it will occupy

$$\frac{5}{245} \times 3 \times 22.4 \times \frac{760}{740} \times \frac{273 + 15}{273} = 1.49 \text{ litres.}$$

*Example 2.*—Find the weight of 1 litre of nitrogen at S.T.P.

The formula of nitrogen is  $\text{N}_2$ , hence its molecular weight is  $2 \times 14 = 28$ . Therefore, since 1 mol, 28 grams, will occupy 22.4 litres at S.T.P., the weight of 1 litre at S.T.P. will be  $28/22.4 = 1.250$  grams. This is the normal density (p. 121), and the theoretical normal density of any gas is = mol. wt./22.4, in grams per litre.

*Example 3.*—Find the weight of 20 litres of carbon dioxide at  $14^\circ \text{C}$ . and 729 mm.

$$\text{Vol. of 20 litres at S.T.P.} = 20 \times \frac{729}{760} \times \frac{273}{287} = 18.25 \text{ litres.}$$

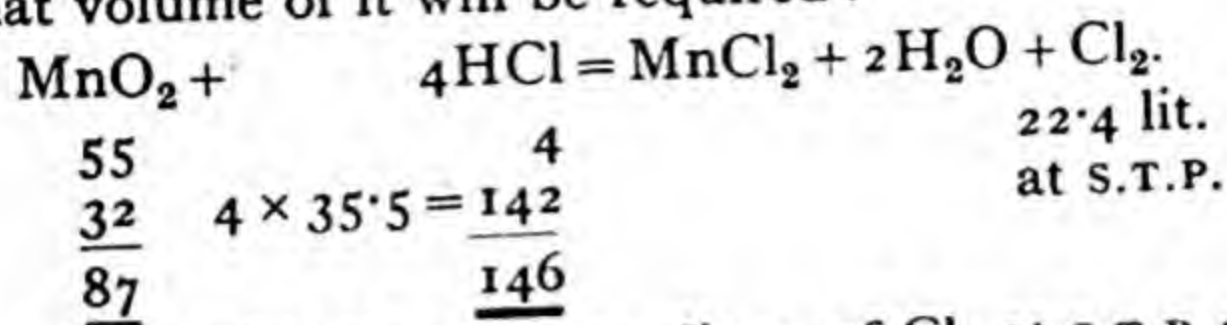
Now 22.4 litres of carbon dioxide ( $\text{CO}_2$ ) at S.T.P. weigh

$$12 + 32 = 44 \text{ grams;}$$

$$\therefore \text{weight of 18.25 litres at S.T.P.} = \frac{18.25}{22.4} \times 44 = 35.85 \text{ grams.}$$



**Example 4.**—What volume of chlorine, measured at  $12^{\circ}$  and 780 mm. pressure, can be obtained from 110 grams of manganese dioxide by treatment with concentrated hydrochloric acid? If the acid contains 38 per cent. HCl and has a specific gravity of 1.2, what volume of it will be required?



$\therefore$  87 grams  $\text{MnO}_2$  give 22.4 litres of  $\text{Cl}_2$  at S.T.P.;

$\therefore$  110 grams  $\text{MnO}_2$  give  $\frac{110}{87} \times 22.4 \times \frac{760}{780} \times \frac{285}{273} = 28.81$  litres at  $12^{\circ}$  and 780 mm.

Weight of HCl required =  $110 \times 146/87$  grams. For every 100 grams of aqueous acid there are 38 grams of HCl;  $\therefore$  weight of aqueous acid required

$$= \frac{110 \times 146 \times 100}{87 \times 38} \text{ grams,}$$

and its volume will be  $\frac{110 \times 146 \times 100}{87 \times 38 \times 1.2} = 405$  c.c.

**Diffusion of gases.**—When a small quantity of a strong smelling liquid such as ether or ammonia solution is spilled in one part of a room, the odour of the vapour is soon perceptible all over the room, and the same effect is noticed with an escape of coal gas. The effect is not due to the motion of the gas or vapour by draughts, as it takes place even in quite still air. It is called **diffusion**, and is due to the motion of the molecules (p. 167); see also p. 176.

The hydrogen, contained in an open *inverted* jar rapidly diffuses out, and air enters; this movement takes place in opposition to gravity, since hydrogen, the lighter gas, moves downwards and air, the heavier gas, moves upwards. Döbereiner in 1823 found that hydrogen confined over water in a cracked flask escaped into the surrounding air, the water rising in the neck of the flask. Graham, a native of Glasgow, who became professor of chemistry at University College, London, showed that as the hydrogen escaped, air entered the flask, and since the pressure inside is reduced, it follows that the hydrogen diffuses out more rapidly than air diffuses in. If the flask was covered with a bell-jar of hydrogen, no change in the level of water occurred.

Graham devised a more convenient apparatus for measuring the rates of diffusion of gases, consisting of a glass tube closed at one end with a thin plug of plaster of Paris. This tube is filled with hydrogen over mercury (Fig. 125). The mercury rises in the tube, and the latter may be sunk in a



FIG. 124. THOMAS GRAHAM, 1805-1869.

jar of mercury so as to keep the level constant. After a certain time all the hydrogen diffuses out, and the tube contains only air which has diffused inwards. No further change of color then occurs. If the volume of residual air is measured, it gives the volume diffusing in the same time as the whole of the hydrogen originally contained in the tube. The inverse ratio of these *volumes* gives the ratio of the *times* required for the diffusion of equal volumes. In this way Graham found the following law of diffusion: the velocity of diffusion of a gas is



inversely proportional to the square root of its density. This is known as Graham's law (1833).

*Example.*—One hundred c.c. of hydrogen are confined in a diffusion tube exposed to air. When change of volume ceases, what volume of air will be left in the tube?

The volumes diffusing are inversely proportional to the square roots of the densities;

$$\therefore \frac{\text{volume of hydrogen}}{\text{volume of air}} = \frac{\sqrt{1.293}}{\sqrt{0.09}};$$

$$\therefore \text{vol. of air} = 100 \times \frac{\sqrt{0.09}}{\sqrt{1.293}} = 26.4 \text{ c.c.}$$

The phenomenon of diffusion may be illustrated by the apparatus shown in Fig. 126. A porous clay pot, such as is used in batteries, is fitted by a rubber bung to a tube passing into a Woulfe's

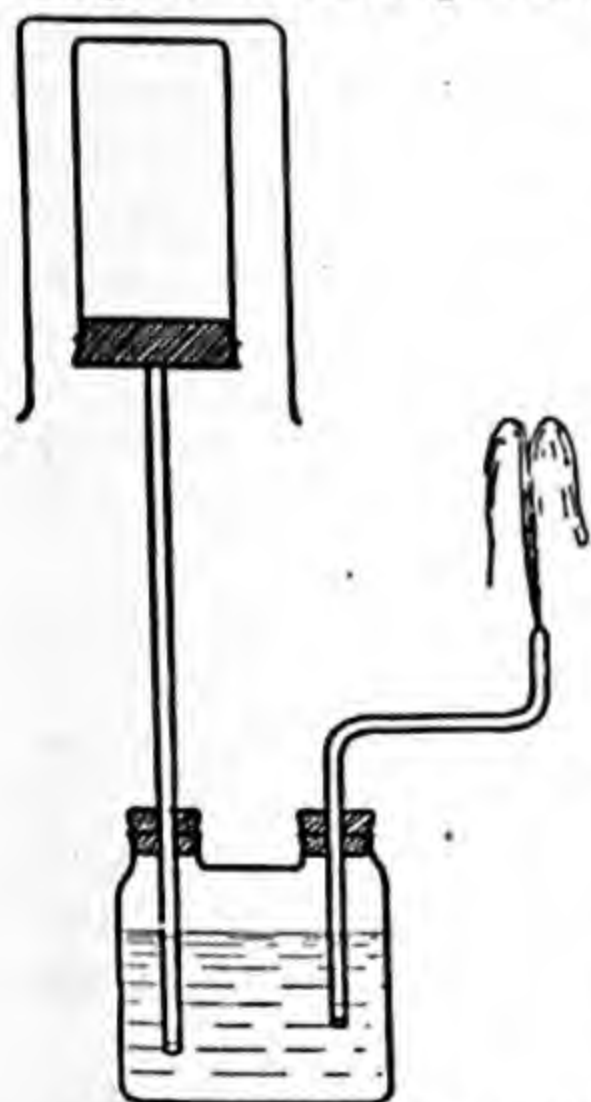


FIG. 126.—DIFFUSION OF HYDROGEN THROUGH A POROUS POT.

bottle containing coloured water, as shown. Dipping into the coloured water is a glass tube drawn out to a jet above. If a large beaker of hydrogen is inverted over the clay pot, hydrogen diffuses into the latter more rapidly than air passes out, and the increase of pressure causes the water to issue from the jet in the form of a fountain. If the beaker is now removed, hydrogen inside the porous pot diffuses out into the air more rapidly than air enters, so that the pressure is reduced. Coloured water thus rises in the vertical tube attached to the porous pot.

**Dissociation.**—Avogadro's law applies to mixed gases as well as to pure gases: the *total* number of molecules in a given volume of air is the same as the number of molecules in an equal volume of pure oxygen or nitrogen. In the first

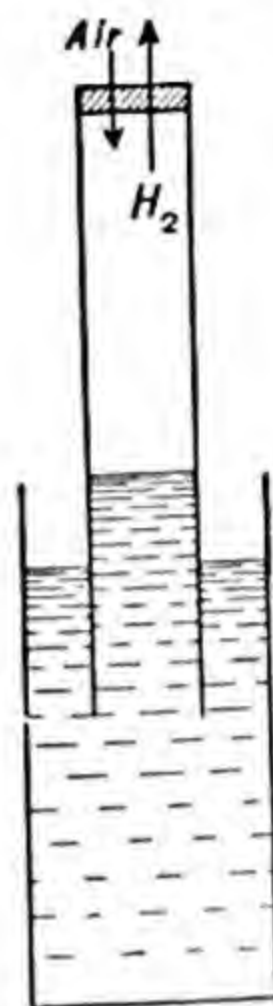


FIG. 125.—GRAHAM'S APPARATUS FOR COMPARING THE RATES OF DIFFUSION OF HYDROGEN AND AIR.

applications of the law to the determination of molecular weights, some difficulty was experienced with certain substances, of which **ammonium chloride** (sal ammoniac) is typical. This salt is produced by the direct union of ammonia,  $\text{NH}_3$ , with hydrochloric acid,  $\text{HCl}$ , and its simplest formula is thus  $\text{NH}_3, \text{HCl}$ , or  $\text{NH}_4\text{Cl} = 53.5$ . Bineau, however, found its vapour density to be only 13, giving a molecular weight of 26. This is roughly half the least possible theoretical value, and corresponds with the formula  $\text{N}_2\text{H}_2\text{Cl}_2$ . This led Deville to question the validity of Avogadro's law, but the true explanation was put forward simultaneously

and independently by Cannizzaro, Kopp, and Kekulé in 1857-58.

They assumed that ammonium chloride, on heating, decomposes into ammonia and hydrogen chloride:



*which recombine on cooling.* The density would then, for complete decom-

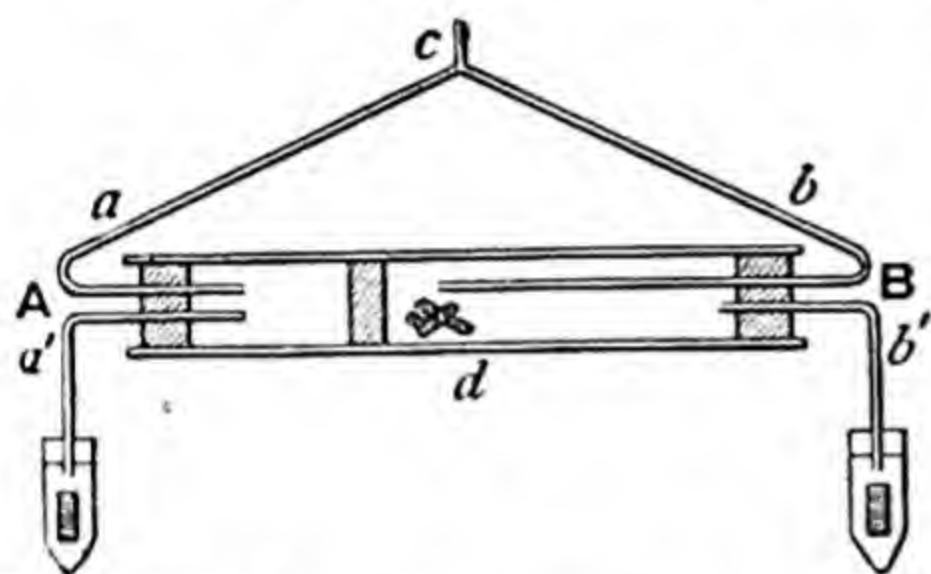


FIG. 127.—APPARATUS TO DEMONSTRATE DISSOCIATION.

position, be half the theoretical density, because the decomposed gas occupies double the volume it would if no decomposition had taken place. *When a substance decomposes on heating and the products recombine on cooling, the process is called dissociation.*

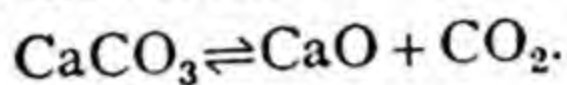
Pebal (1862) was able to demonstrate the dissociation by separating ammonia and hydrochloric acid from the vapour by diffusion. Ammonia is much lighter than hydrochloric acid and therefore diffuses more rapidly (*cf.* p. 163).

A piece of ammonium chloride is heated in a tube *d* divided into two parts by a porous plug of asbestos (Fig. 127). The ammonia diffuses through the plug more rapidly than the hydrogen chloride, so that the gas in the part *Ad* becomes alkaline, and that in the part *Bd* becomes acid (from the excess of hydrogen chloride present). By blowing out the gases from the two parts of the tube through tubes containing pieces of litmus paper (*a'* and *b'*) this may be demonstrated.

In dissociation the change may be incomplete, so that a state of chemical equilibrium is established, in which the dissociating substance and the products of dissociation are all present:



$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$ . The extent of dissociation increases gradually as the temperature rises, and at a sufficiently high temperature may become complete. The dissociation of ammonium chloride is applied in the use of this substance as a flux in soldering. At the high temperature the salt is dissociated, and the hydrochloric acid, by removing the oxidised surface of the metal, enables the solder to adhere. The production of quicklime from limestone is also an example of dissociation :



(See again the distinctions between chemical and physical changes, p. 49.)

**\*The kinetic theory of gases.**—The properties of gases which have previously been considered (Boyle's law ; expansion by heat ; Avogadro's law ; diffusion) are all explained by a theory of the gaseous state known as the **kinetic theory of gases**, first suggested by Bernoulli in 1738, but developed mainly in the nineteenth century. The fact that a liquefied gas occupies only a small fraction of the bulk of the gas, proves that *the molecules in a gas are widely separated*. When a gas is compressed, the molecules move closer together.

**Liquids and solids** are compressed only by the application of very large forces, and then only slightly. Their molecules are no doubt already closely packed, with only a small amount of free space between them. Since the molecules of solids and liquids do not tend to separate and spread through any volume available for them, as is the case with the molecules of gases, they are supposed to be held together by an attractive force called **cohesion**. In gases there is very little cohesion between the molecules unless they are fairly close together, as when the gas is strongly compressed. The cohesive forces may then become appreciable, especially if the gas is also strongly cooled, and the molecules may coalesce to form a liquid.

The molecules of a gas do not tend to settle out on standing, and the mixing or diffusion of gases (p. 161) shows that *the molecules of a gas are in motion*. This assumption constitutes the kinetic theory of gases (from the Greek *kinesis*, motion). It is, of course, impossible to demonstrate the existence of this motion directly, since the molecules are far too small to be seen, but the results of the assumption are in agreement with experiment.

**\*Gaseous pressure.**—It is easy to explain the *pressure of a gas* on the kinetic theory, since it is regarded as the result of *collisions*

of the molecules with the sides of the containing vessel. Since the pressure does not diminish with time, the molecules must be perfectly elastic, so that they rebound on striking the wall, or on colliding with one another, with undiminished kinetic energy. If they were not elastic they would gradually come to rest and the pressure would vanish.

When a gas is compressed, its molecules are crowded together, so that there is a greater number in a given space. Their speeds are not altered if the temperature remains the same. The particles will, therefore, collide more frequently with the walls of the vessel, and the pressure will increase. The diagrams of Fig. 128 show that when the volume is reduced to one-half and

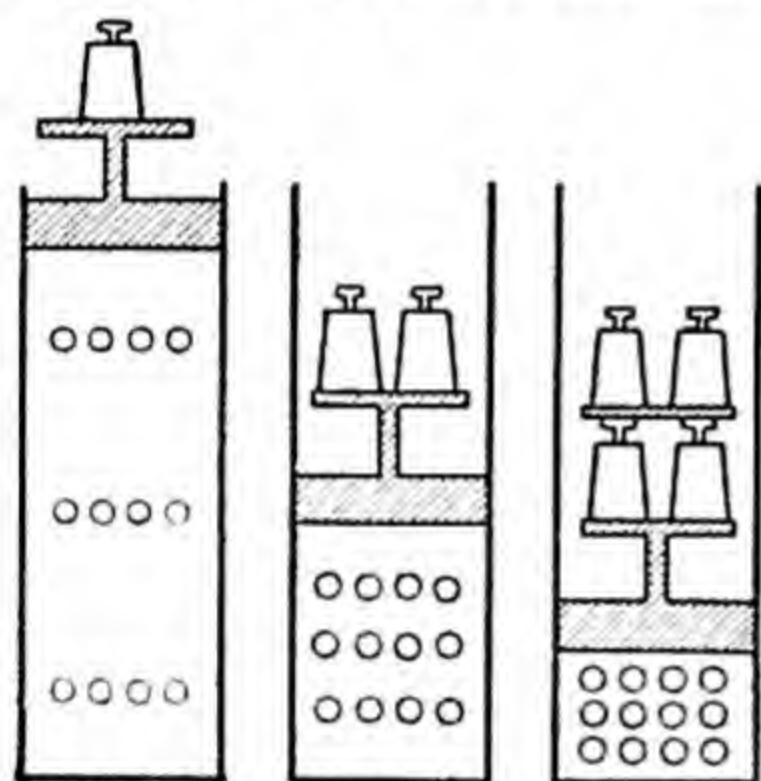


FIG. 128.—COMPRESSION OF A GAS:  
BOYLE'S LAW.

one-quarter, respectively, there will be twice and four times the number of molecules in the given space, and thus there will be twice or four times the number of collisions per second as in the gas at the original volume. *The pressure is therefore inversely proportional to the volume*, as Boyle's law requires. This result was deduced by Bernoulli in 1738.

If a gas is heated in a vessel so that the volume remains constant, the pressure increases. Since the number of molecules remains the same per unit volume, their speed must have increased so as to produce more collisions per second. The effect of temperature on a gas is explained in terms of the kinetic energy of the molecules. Heat is a form of kinetic energy, and when a gas is heated whilst its volume remains constant, the heat absorbed goes to increase the kinetic energy of each particle of the gas. The kinetic energy of a molecule of mass  $m$  is  $\frac{1}{2}mv^2$ , where  $v$  is the velocity. Hence the velocity of the particles is increased when their kinetic energy is increased, and therefore both the frequency of the collisions with the walls and also the force exerted by each colliding particle will increase. The pressure, therefore, will increase with rise of temperature at constant volume, as is found to be the case. At the absolute zero, the molecules would have no kinetic energy and the pressure would be zero.



**\*Velocity and free path of gas molecules.**—Since the particles of a gas are acted upon by gravity, there will be a tendency for them to settle to the lowest part of the gas, but, in a small volume of gas, this is almost completely overcome by the motion of the molecules, which dart about in all parts of the gas and tend to keep it uniformly mixed. In a very tall column of gas there is, however, an appreciable settling out due to gravity, and this is the reason why the atmosphere becomes more and more rarefied as we ascend from the surface of the earth. In a mixture of gases there will also be a tendency for the heavier molecules to cluster together nearer the bottom of the column and the lighter at the top, so that in the upper layers of the atmosphere there is probably more nitrogen than in the lower parts, which contain relatively more oxygen. At a height of 30 miles it is calculated that there are 8 volumes of nitrogen to 1 of oxygen, instead of 4 to 1 as on the surface of the earth. At a height of 70 miles perhaps only the lightest gas, hydrogen, is present, though there is practically no hydrogen at sea-level.

The velocity of gaseous molecules depends, at a given temperature, on the weight of the molecules, the heavier molecules moving more slowly than the lighter, as will be explained later. In oxygen (or air) at the ordinary temperature, the molecules are darting about with speeds of about a mile a second, *i.e.*, about as fast as a rifle bullet. Each particle moves in a straight line until it collides with another particle, or with the walls of the vessel, when it starts off in a straight line in another direction. The *average distance* through which a molecule moves between a collision with another molecule and the next collision is called the **mean free path**. It depends on the pressure, and will clearly be smaller the higher the pressure, since the molecules are then closer together. In air at atmospheric pressure the mean free path is only about a ten thousandth of a millimetre ( $10^{-5}$  cm.). If all the free paths of an oxygen molecule are joined so as to make up 1 mile, which is the distance traversed per second, 4000 million of them ( $4 \times 10^9$ ) will be required, and this clearly gives the number of collisions per second.

**\*Energy of gas molecules.**—The heat supplied to a gas will, generally, be used not only to increase the kinetic energy of the molecules due to their motion in straight lines (which is the only effect when the molecules consist of single atoms, as in mercury vapour and argon, which are *monatomic* gases) but also to increase the kinetic energy due to the *rotation* of the molecules. This is like the energy of a spinning wheel. For



example, a molecule of hydrogen, oxygen, etc., composed of two atoms, may be pictured as a very minute dumb-bell, and this is not only hurtling through space with a speed of over a mile a second at the ordinary temperature but is also spinning; its motion will resemble that of a dumb-bell which had been held by one knob and then violently thrown into the air. In more complicated molecules the atoms may also vibrate, like two balls connected by a spring, and this *vibration* will also absorb kinetic energy. All these contributions go to make up the **heat energy of a gas**. It is obvious that we can obtain some idea of the complexity of the molecules of a gas from its **specific heat**, which is the energy absorbed per  $1^\circ$  rise in temperature, and this method has been used with the inert gases, which form no compounds (p. 398), to find the atomic weight, which is identical with the molecular weight.

Graham's law of diffusion also follows from the kinetic theory. If we have two gases at the same temperature and the same pressure, the kinetic energies of their molecules will be equal. Thus  $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$ ;  $\therefore v_1/v_2 = \sqrt{m_2/m_1}$ , *i.e.*, the velocities of the molecules are inversely proportional to the square roots of the molecular weights, *i.e.*, of the densities. The velocity of diffusion, however, is clearly proportional to the velocity of the molecules, hence Graham's law results.

The fact that all gases obey the same laws relating to pressure, volume and temperature is explained by Avogadro's hypothesis, since equal volumes contain equal numbers of molecules, the latter being widely separated.

**\*The molecular structure of liquids.**—Some idea of the molecular structure of liquids has already been given. The molecules are now closer together than in a gas, and are practically in contact. Diffusion takes place in liquids just as it does in gases, as can be shown by placing some crystals of a coloured salt such as copper sulphate at the bottom of a tall cylinder of water and noting that the colour due to the dissolved substance slowly spreads through the column of water (Fig. 34). The molecules of a liquid are therefore in motion, but since they are nearly in contact, this motion will be different from that of gas molecules. The liquid molecules will be gliding over one another much as live eels squirm about in a basket. It has been calculated that only about one-third of the volume of a liquid is not occupied by the molecules, so that the motion will be correspondingly restricted.

When the liquid is heated, some of the molecules acquire so



much kinetic energy that they can break away from the cohesive attraction of the other molecules in the liquid and start away on a voyage through the space above the liquid. They have now become gas molecules and this is what happens in the **evaporation** of a liquid. The state of affairs is somewhat like that pictured in Jules Verne's story, when a projectile is shot from a gun with such velocity (really the kinetic energy is the determining factor) that it will escape from the gravitational attraction of the earth and pass away into space.

When a molecule of vapour which is approaching the liquid comes near it, the cohesive force again asserts itself, and the molecule is dragged into the liquid. This is **condensation**. When as many molecules enter as leave the liquid in a given time, there is equilibrium, and the vapour is then saturated (p. 43).

It is also considered that in **solutions** the molecules of solvent and solute are in motion. The dissolved substance is dispersed in the form of particles of molecular size which do not settle out on standing, since they are in motion, and cannot be filtered off, since they pass with the solvent particles through the pores of the filter.

The consideration of the structure of solids is deferred to a later chapter (p. 183).

**\*Counting and weighing atoms and molecules.**—Although Dalton's atomic theory, Avogadro's hypothesis and the kinetic theory of gases were used by chemists and physicists throughout the nineteenth century, and although the results of experiment were in agreement with the predictions of theory, there seemed little possibility that any more direct indication of the existence of atoms and molecules would ever become available. In spite of the fact that calculations by different methods of the number of molecules in 1 c.c. of a gas had given results in surprisingly good agreement, some chemists were more and more inclined to insist on the hypothetical character of the atomic theory. With the opening of the twentieth century, a great flood of new knowledge on the atomic constitution of matter surged into physics and chemistry, and at the present day the existence of atoms is regarded as firmly established: the consideration of the inside of the atom is the present problem, and from the structure of matter science has passed in a giant's stride to the structure of atoms.

This great advance became possible with the discovery by Madame Curie of **radium** and the intensive study of radio-activity by Rutherford and others. The atom of the element



radium differs from such atoms as oxygen in its liability at any time to undergo a devastating disruption and explosion, in which the *débris* resulting from the ultramicroscopic cataclysm is hurled away with immense speed. One of these tiny fragments of the exploded atom is a positively charged atom of helium, called an  $\alpha$ -particle. These  $\alpha$ -particles are ejected with speeds 100,000 times faster than a swift rifle bullet, and they possess enormous kinetic energies as compared with gas molecules.

Rutherford and Geiger in 1908 devised a method of making each separate  $\alpha$ -particle reveal its presence. It is allowed to fly into a gas at low pressure. It then collides with the molecules of the gas, and the impact is so severe that the outer particles of negative electricity, or electrons (p. 239), which are present in the atoms of the gas, are knocked out of the molecule. The gas now contains the positive residues of the atoms from which the negative electrons have been ejected, and negative particles formed by the association of these negative electrons with gas molecules. A great number of such charged gas molecules, or ions, is produced before the energy of the  $\alpha$ -particle is exhausted, and *the gas becomes a conductor of electricity*, since the ions can move in an electric field. The conductivity produced by a *single*  $\alpha$ -particle can be detected.

The apparatus used by Rutherford and Geiger consisted of a long glass tube,  $AA'$  (450 cm. long and 2.5 cm. wide), called the 'firing tube' (Fig. 129), which was exhausted, and contained on a lead plate,  $a$ , at the end  $A$  a preparation of radium, which expelled  $\alpha$ -particles. Some of these shot along the tube and passed through the narrow tube,  $B$ , into the brass chamber  $C$ , where the gas at low pressure was rendered conducting. A mica window at  $F$  shut off the gas from the evacuated tube,  $AA'$ . Running through the vessel  $C$ , and insulated from it by the ebonite ends, was a metal wire,  $w$ , which was connected through a battery and electrometer to the outer surface of the brass vessel. As each  $\alpha$ -particle entered the chamber (at the rate of about one every second), it made the gas conducting, and the electrometer gave a deflection. In this way the individual  $\alpha$ -particles passing into  $C$  could be counted. Since it was shown by separate experiments that each  $\alpha$ -particle turns into an atom of helium gas, and since the volume of helium gas given off by the radium preparation in a given time could also be found by experiment, all the data required were known.\* We have simply

\* Allowance is made, of course, for the fact that only a small, calculable, fraction of the  $\alpha$ -particles emitted by  $a$  pass through  $F$ .



to find how many  $\alpha$ -particles would go to form 22.4 litres of helium at s. t. p., and this gives us the number of molecules in a gram-molecule, the same for all gases. The result is  $6 \times 10^{23}$  and is called **Avogadro's constant**.

This is an enormous number: it corresponds with  $3 \times 10^{19}$  molecules per c.c. and the imagination cannot cope with it. We can, however, imagine the molecules in this 1 c.c. of gas passing out one by one through a small aperture at the rate of one million per second, and it would then take one million years for them all to pass out. Think how many atoms there are in the solar system!

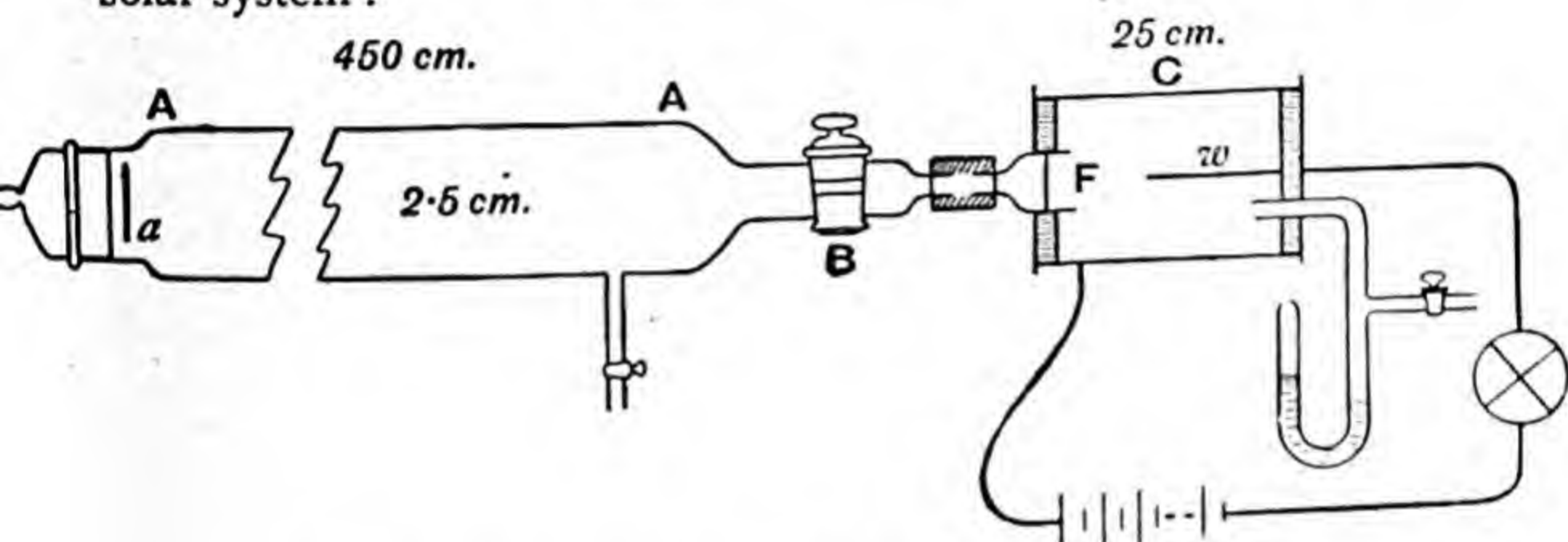


FIG. 129.—RUTHERFORD AND GEIGER'S APPARATUS.

Molecules are extremely minute: the diameter of the hydrogen molecule is about  $2 \times 10^{-8}$  cm. The smallest distance which can be perceived with a powerful microscope is about 0.0002 mm., and it is surprising that this would contain only about 1000 hydrogen molecules placed in line. Thus the molecules are not so greatly removed from visibility as we might imagine from the vast number per cubic centimetre. If we could increase the power of the best modern microscope rather less than a thousand-fold, we should see large molecules quite easily, provided the usual laws of optics held good.

We can now calculate *the weight of an atom of hydrogen*. Two grams of hydrogen contain  $6 \times 10^{23}$  molecules, each containing two atoms. Hence each atom weighs

$$1 \div 6 \times 10^{23} \text{ gm.} = 1.66 \times 10^{-24} \text{ gram.}$$

To find the weight of any other atom or molecule we have simply to multiply this number by the atomic or molecular weight of the substance. The absolute weights of all atoms and molecules are known.

The *absolute* weights of atoms have also been found by other methods and the results are in excellent agreement. The *absolute* weight of a *single atom* of oxygen can be determined with greater accuracy than the equivalent of oxygen can be found experimentally by a fairly experienced student of chemistry. Aston (1926) has found the *relative* masses of *single atoms* of some elements with an accuracy nearly as great as that attainable by the most experienced workers on atomic weights, whose methods and skill exceed anything else possible in the chemical laboratory.

### \*MOLECULAR WEIGHTS IN SOLUTIONS.

**Osmotic pressure.**—The diffusion of dissolved substances shows that the molecules of the dissolved substance are moving about

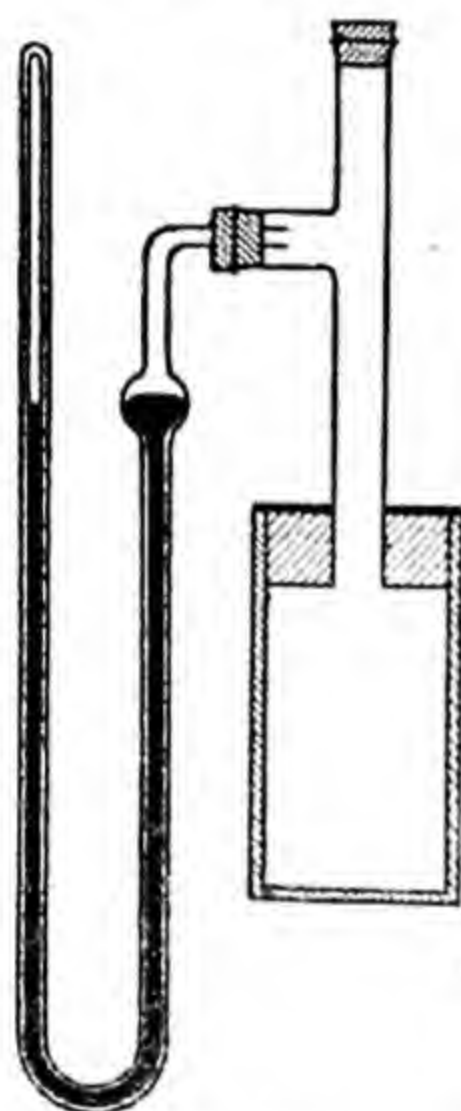


FIG. 130.  
OSMOTIC PRESSURE  
APPARATUS.

and colliding with liquid molecules, and as a result of these collisions the rate of diffusion is slow. If we could imagine a partition placed over the solution below so as to divide it from the water above, both water molecules and those of the dissolved substance would strike against it. Let us now suppose that the water molecules can pass freely through the partition in both directions, like flies through the netting around a tennis court, but the molecules of the dissolved substance cannot pass through, but strike the partition and are reflected back again, like the tennis balls. Such a partition can be realised by depositing a film of a slimy amorphous substance, copper ferrocyanide, in the walls and pores of a porous pot, and is called a semipermeable membrane. The dissolved substance exerts a pressure on the semipermeable membrane which is called an **osmotic pressure**. When the pot is filled with a solution, say of sugar, and is fitted with a tight stopper and a manometer (Fig. 130), the pressure produced when the pot is placed in water is measurable and is the osmotic pressure of the solution.

Van 't Hoff in 1885, on the basis of such experiments made in 1881 by Pfeffer, a botanist, showed that *the osmotic pressure exerted by a dissolved substance is equal to the pressure which would be produced by the same number of molecules of a gas*



confined in a space equal to the volume of the solution, and at the same temperature. This is true only when the solution is dilute.

The result provides a means of determining the molecular weight of a substance in solution.

Suppose we have a solution of cane sugar in water containing 1 per cent. of sugar. At a temperature of  $14^{\circ}\text{C}$ . this exerts an osmotic pressure of 51 cm. of mercury. Let  $x$  be the molecular weight of the sugar, then we shall have  $1/x$  gram-molecules in 100 c.c. or  $10/x$  per litre. If the sugar behaved as a gas, one gram-molecule in 22.4 litres at  $0^{\circ}\text{C}$ . would exert a pressure of 1 atm., or in 1 litre at  $0^{\circ}\text{C}$ . it would exert a pressure of 22.4 atm., or  $22.4 \times 76$  cm. of mercury. At  $14^{\circ}\text{C}$ . the pressure would be  $22.4 \times 76 \times \{(273 + 14)/273\}$  cm. of mercury. Since the pressure is proportional to the number of molecules in a given space (Boyle's law), the pressure due to  $10/x$  gram-molecules in a litre would be  $\frac{10}{x} \times 22.4 \times 76 \times \frac{287}{273}$  cm. and this will be equal to 51 cm. From the equation :

$$\frac{10}{x} \times 22.4 \times 76 \times \frac{287}{273} = 51,$$

we find, on solving for  $x$ , the value 350 for the molecular weight of cane sugar. The formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  gives 342.

Osmotic pressure plays an important part in plant and animal life. The liquid in the cells of plants contains dissolved substances, and outside this is a lining of protoplasm which acts as a semipermeable membrane. When the cells are immersed in a concentrated salt solution, water passes from the cell to the solution and the protoplasm shrinks away from the cell wall. When placed in pure water, the latter enters the cell and swells it. A solution having the same osmotic pressure as that in the cell, even though the pressure is due to a different dissolved substance, produces no change, and such solutions with equal osmotic pressures are called isotonic. In physiology, a salt solution having the same osmotic pressure as the blood is called a *physiological saline solution*: it does not produce any effect on the cells of the blood corpuscles.

Measurements of osmotic pressure are difficult, and are not often used in the determination of molecular weights in solutions. Instead, a method which is really closely connected with osmotic pressure is often used, viz. the measurement of the freezing point of a solution.

The osmotic pressure may be considered as the pressure which must be applied to a solution to squeeze pure water out through the walls of the containing semipermeable pot. The separation of pure water, leaving a more concentrated solution in the pot, therefore calls for *the expenditure of work*, say in pressing down a piston working inside the porous pot. Another way of separating pure water from the solution is by freezing it, since the ice which separates (provided the solution is not too concentrated) is quite free from the dissolved substance, which remains in the solution and so makes it more concentrated (p. 40). The freezing of pure water may be caused by refrigerating apparatus, requiring some kind of motor to drive it, and to freeze the solution will require still more work to be performed by the motor, since the work of separating water from the solution must be added. In other words, we should expect the freezing point of a solution to be lower than that of pure water, and this is found by experiment to be the case.

**Molecular weights from freezing points.**—Every pure liquid freezes at a definite temperature, called its **freezing point**. The solid melts again at the same temperature, so that the **melting point** is the same as the freezing point. It is true that a liquid may often be *supercooled* several degrees below its freezing point, but if a trace of solid is added, solidification begins, when the temperature rises to the freezing point and remains there till all the liquid is frozen.

If a substance is dissolved in the pure liquid, the freezing point of the latter is lowered. As we have explained, this is utilised in countries where winter temperatures are severe, as in Canada, to prevent the freezing of water in motor car radiators: glycerin is added to the water, and the solution remains liquid far below the temperature at which water would freeze. The same effect is produced by adding alcohol, but this is less convenient, since the alcohol is volatile and tends to escape when the liquid is heated up during the running of the engine. Equal weights of glycerin and alcohol dissolved in equal weights of water lower the freezing point of the latter differently: the alcohol has a greater effect in producing a lowering of freezing point than the glycerin.

A very important result was discovered by Raoult in 1883: if equal fractions of the *molecular* weights of alcohol and glycerin are dissolved in water, the solutions freeze at the same temperature. This is a general law for a great number of substances, viz. non-electrolytes, or substances which do not form conducting



solutions when dissolved in water. *Weights of non-electrolytes which are in the ratio of the molecular weights, when dissolved in equal weights of water, produce the same lowering of freezing point.*

Electrolytes always produce an abnormally large depression, owing to the fact that in solution they are split up into ions, and each of the latter behaves as an independent molecule (p. 208).

Raoult's discovery enables us to find the molecular weights of many substances which cannot be volatilised without decomposition. It is known from experiment that, *for the same substance, the depression of freezing point is proportional to the concentration* (Blagden's law). The depression produced by 1 gram-molecule dissolved in 1000 grams of water is  $1.86^\circ$ , for all non-electrolytes. Hence, if we find the depression produced for a solution of known concentration, we have only to calculate by proportion the number of grams of substance which must be dissolved in 1000 grams of water to produce a lowering of  $1.86^\circ$  and this will be the molecular weight of the dissolved substance.

*Example.*—0.1834 gm. of hydrogen peroxide dissolved in 17.607 gm. of water gave a solution freezing at  $-0.571^\circ$ . Weight of peroxide in 1000 gm. of water  $= 0.1834 \times \frac{1000}{17.607} = 10.42$  gm.

Therefore, 10.42 gm. of peroxide in 1000 gm. of water cause a lowering of freezing point of  $0.571^\circ$ . What weight will cause a lowering of  $1.86^\circ$ ? Since the lowering is proportional to the concentration, this weight will be

$$10.42 \times \frac{1.86}{0.571} = 33.9 \text{ gm ;}$$

$\therefore$  molecular weight of hydrogen peroxide = 33.9. ( $\text{H}_2\text{O}_2$  requires 34.)

The apparatus used for the determination of the freezing point of a solution is shown in Fig. 131. The weighed amount of water (or other solvent, each solvent having a special *molecular depression* instead of  $1.86^\circ$ ) is contained in the inner tube. This is enclosed in a wider tube, which in turn is immersed in a freezing mixture in an outer jar. The object of the air jacket between the two inner tubes is to make the cooling slow, so that accurate readings may be made. The liquid is stirred, and the temperature at which the mercury in the sensitive *Beckmann's thermometer*

becomes steady after falling is read off. A weighed amount of the substance is then introduced through the side arm in the inner tube, dissolved, and the process repeated.

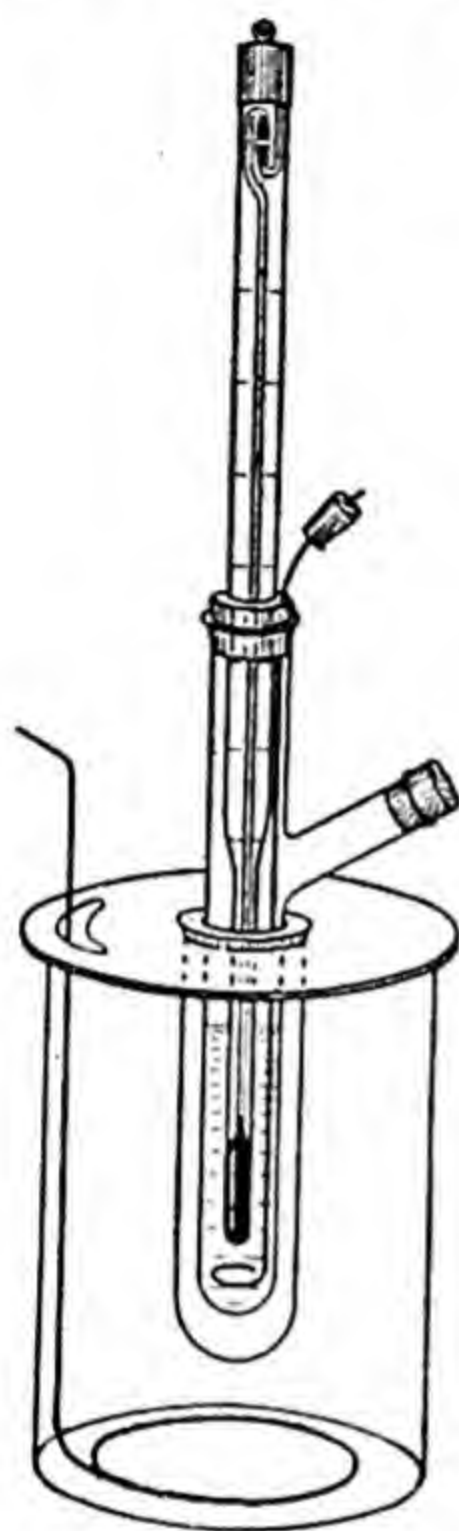


FIG. 131.—BECKMANN'S APPARATUS

FOR DETERMINING THE MOLECULAR WEIGHT OF A DISSOLVED SUBSTANCE FROM THE LOWERING OF THE FREEZING POINT OF THE SOLVENT.

Raoult's method does not enable us to find the molecular weight of the solvent, or in fact that of any *pure liquid*. There is no very satisfactory method of determining the molecular weights of liquids: one method depends on the measurement of the rise in a capillary tube at different temperatures. Many liquids contain simple molecules, but others, such as water, are associated, *i.e.*, contain clusters of simple molecules, in water perhaps  $(H_2O)_3$ .

**Colloids.**—By examining the rates at which dissolved substances diffuse into water (p. 31), Thomas Graham, whose work on diffusion of gases was described on p. 161, found in 1849 that some substances diffuse fairly rapidly and others very slowly. Salts, acids, and bases are rapidly-diffusing substances; gum, gelatin and albumin (white of egg) diffuse very slowly. There is a rather sharp line of demarcation: the gelatin, gum and albumin diffuse *very* slowly indeed! The rapidly diffusing substances, mostly crystalline in the solid state, were called **crystalloids** by Graham. Gum and albumin, which form amorphous solid masses resembling glue, were called **colloids** (Greek *kolla*, glue). The differences were so great that Graham considered himself justified in differentiating between 'two worlds of matter, the crystalloid and the colloid,' each with characteristic properties.

If we pour a solution of potassium iodide and starch into a dialyser (Fig. 132) consisting of a piece of parchment paper tied tightly over the mouth of a bell-jar, suspend the bell-jar with the parchment paper dipping into distilled water in a dish, and after half an hour add chlorine water to the water in the dish, a yellow colour, due to liberated iodine, shows that the iodide has diffused



through the parchment paper, but the starch is retained, since this would have given a blue colour with the iodine, as may be seen by adding chlorine water to the liquid in the bell-jar.

The *sharp* differentiation between crystalloids and colloids made by Graham, although it is of practical significance, has not been confirmed as a general principle. Albumin may be obtained in a crystalline form, and crystalline substances, such as common salt, may also be prepared in the form of colloidal solutions by precipitation in liquids (*e.g.*, ether) in which they do not form true solutions. The real factor determining whether a substance forms a colloidal solution or a true solution we now know to be *the size of the dispersed particles*, as Graham suspected;

it is more correct to speak of the **colloidal state** of a substance than of 'colloidal substances.'

A common example of a **colloidal solution** is milk, which consists of innumerable very small, but microscopically visible, droplets of fat floating in a watery liquid. Colloidal solu-

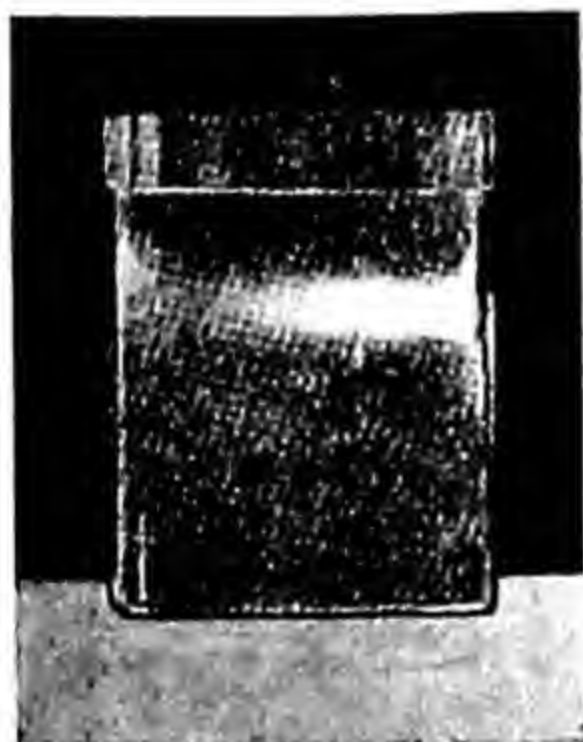


FIG. 133.—TYNDALL CONE, DUE TO THE SCATTERING OF A BEAM OF LIGHT ENTERING AT THE SIDE, BY FINE PARTICLES SUSPENDED IN A LIQUID.

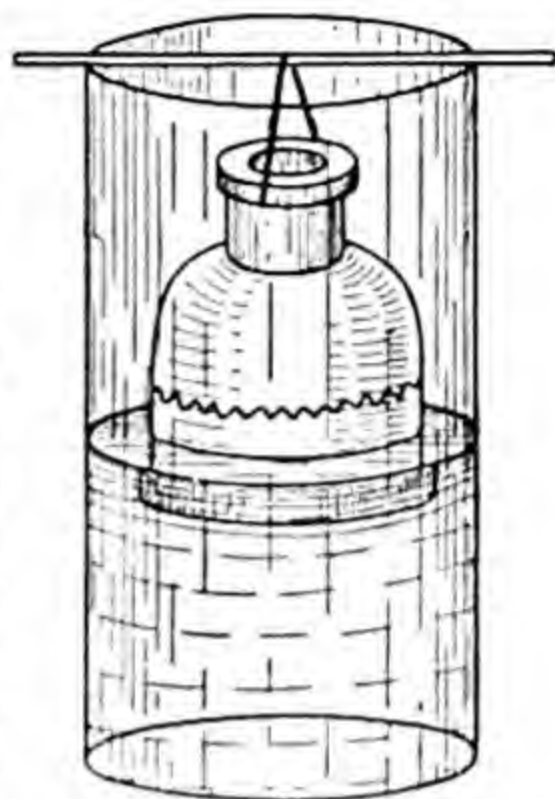


FIG. 132.—GRAHAM'S DIALYSER.

tions all contain particles which are larger than molecules, and often much larger, but usually (unlike fat globules in milk) the particles are not microscopically visible. These are floating about in a medium and do not tend to settle at all easily. Colloids are for this reason sometimes called **dispersed systems**. Tobacco smoke is, therefore, really a colloidal system, containing fine solid particles dispersed in a gas. Fogs and smokes are dispersed systems, the first of liquid droplets in a gas and the second of solid particles in a gas.

Some writers distinguish **true colloids** from suspensions by the circumstance that the dispersed particles in the former are

not microscopically visible. They may be recognised by making use of what is called the Tyndall effect, *i.e.*, the *scattering of light* by small particles (Fig. 133). The minute particles of dust (*motes*) seen in a beam of sunlight are rendered visible in this way, and they then appear much larger than they really are. When a strong beam of light is sent through a colloidal solution,

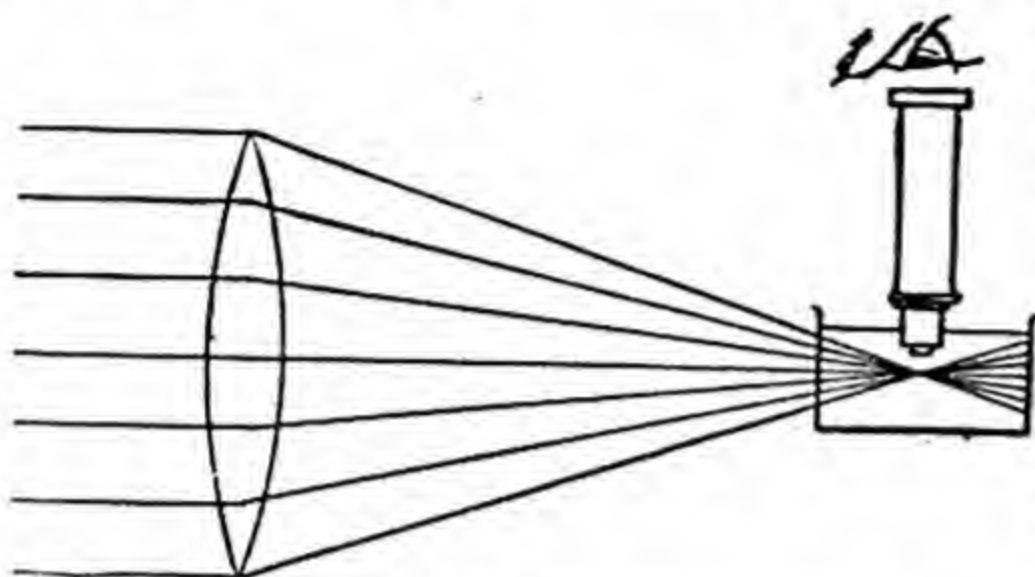


FIG. 134.—ULTRAMICROSCOPE.

then, on looking down on the path of the beam with a microscope, the colloid particles, which cannot be seen at all by light transmitted *through* the solution, become visible as bright points owing to their scattering effect. The apparatus is called an **ultramicroscope** (Fig. 134). The bright points usually have a continuous, zig-zag, tremulous motion called the **Brownian movement**, since it was discovered by the English botanist, Robert Brown, in 1827. It is shown only by very small particles. The actual paths described by a particle undergoing Brownian movement are shown in Fig. 135, from an experiment of Perrin, a French physicist. The light scattered by colloid particles is polarised.

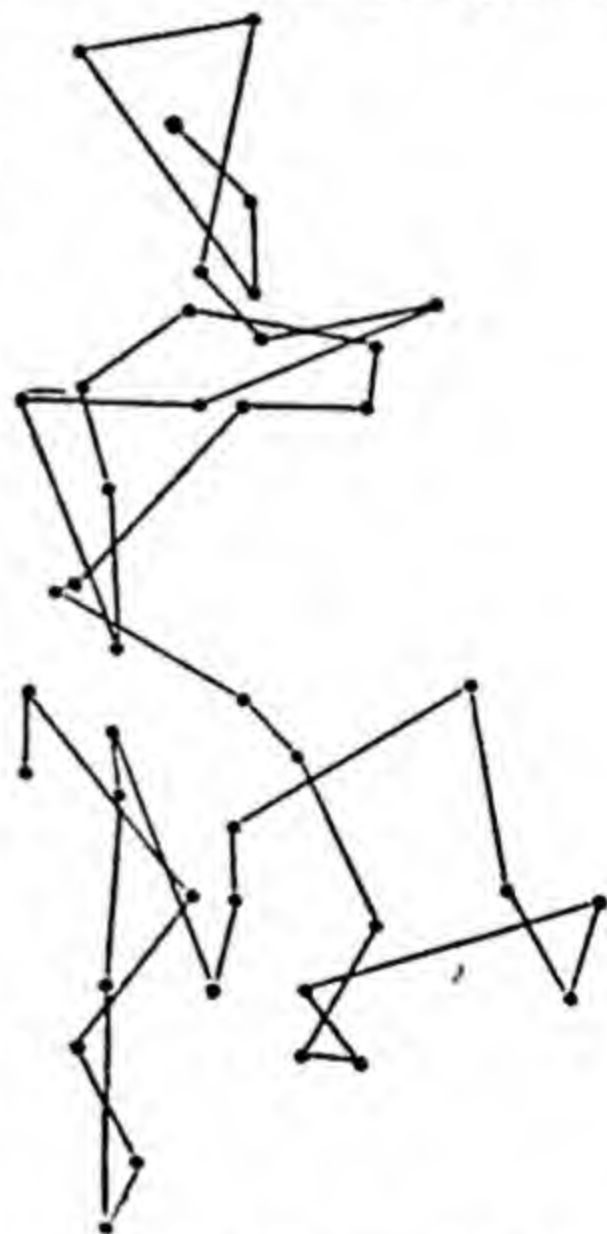


FIG. 135.—PATHS OF A PARTICLE EXECUTING THE BROWNIAN MOVEMENT.

The Brownian movement was explained by C. Wiener in 1863 as follows. The colloidal particle is bombarded on all sides by molecules of liquid striking against it. If the particle were very large, the effect of this bombardment would be the same all over the surface, but if the particle is small there may be more molecules colliding on one side of it at a given instant than on the opposite side. The particle is therefore urged through the liquid by this unbalanced pressure until the



unequal distribution of pressure shifts round and the particle starts off in another direction.

Colloid particles are often *electrically charged*, some positive and others negative. They are precipitated by electrolytes, the charged ions of which neutralise the opposite charge on the colloid particles. The charges on the particles, by mutual repulsion, prevent to some extent the particles clotting together, but when the charges are neutralised this occurs and the colloid is *coagulated*. Ions with large charges, such as the aluminium ion,  $\text{Al}^{+++}$ , are more effective in bringing about coagulation than ions with small charges, such as the potassium ion,  $\text{K}^+$  (see p. 205).

Colloids are common products of plant and animal activities: milk, jelly, glue, rubber latex, white of egg, etc., are examples. In some cases the solutions readily pass by evaporation or simple coagulation into solid or semi-solid masses called *gels*, a name derived from gelatin. Gelatin can form gels of varying consistency, from table jelly to hard glue. Many gums form jellies with water, but some merely swell up and gelatinise without going into solution unless heated. The structure of gels is a disputed point: they seem in many cases to be felted masses of long, hair-like crystals with a liquid enmeshed between them, with an open structure, whilst in others they show no trace of microscopic structure and may be solid solutions. On drying up, the water in the flabby mass evaporates, leaving the skeleton of the gel ready, in many cases, to swell up again when placed in water. Nature seems economical of solids in the vegetable and animal kingdoms: many tissues are largely water associated with colloids to form flexible gels.

Many colloidal solutions depend for their stability on the presence of small amounts of a third substance which keeps the colloid particles dispersed. Salad dressing cannot be made to remain dispersed unless white and yolk of egg are added to the oil and vinegar, and such materials, making colloids stable, perhaps by forming a film over the colloid particles, are called *protectors*: protected colloids are very common. Milk is an emulsion of butter droplets in water, protected by another colloid *casein* (the chief constituent of cheese) and calcium salts. Rubber latex, the milky juice of the tree, is an emulsion of rubber globules protected by an alkali: the rubber is precipitated as *crepe rubber* on adding acetic acid. *Collargol* and *protargol* are protected colloidal solutions of silver used in medicine, e.g., in treatment of eye diseases.

Colloidal solutions of many metals may be obtained by causing an electric arc to pass between two wires of the metal, for example platinum, under water. Very minute particles of the metal are torn off and dispersed through the water to form a colloidal solution. In other cases (*e.g.*, copper, silver, and lead) a salt of the metal is reduced in presence of a protective colloid.

The *surface* exposed by the colloid particles is very large for a given weight. A cube of solid with edges 1 cm. in length exposes a surface of 6 sq. cm. When it is subdivided into eight cubes of edge 0.5 cm. the surface increases to 12 sq. cm., and if the subdivision is carried on until the parts are as small as the particles in colloidal solutions, the area exposed is about six and a half acres. These particles have diameters between 1 and 100 millimicrons, a millimicron ( $m\mu$ ) being one millionth of a millimetre. Particles larger than  $100m\mu$  are microscopically visible, and occur in *suspensions*; particles smaller than  $1m\mu$  are not visible even with the ultramicroscope, and we are then in the region of *true solutions*.



## CHAPTER XI

### ATOMIC HEATS. ISOMORPHISM

**Confirmation of atomic weights.**—In Chapter X a method of finding the multiple of the *exactly* determined equivalent of an element which is equal to its atomic weight has been described, depending on Avogadro's law; there are four other methods by which the approximate atomic weight may be found. These depend on the use of (1) atomic heats; (2) isomorphism; (3) chemical analogies; and (4) the periodic law.

The ratio of the atomic weight of an element to its equivalent is called the **valency** :

$$\text{Valency} = \frac{\text{atomic weight}}{\text{equivalent}}.$$

An element has only one atomic weight, but it may have more than one equivalent, and to each equivalent there is a corresponding valency.

**Dulong and Petit's law of atomic heats.**—The unit of heat, the **calorie**, is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade. The **specific heat** of a substance is the number of calories required to raise the temperature of one gram of the substance through one degree Centigrade.

In 1819 Dulong and Petit, two French scientists, found that the atomic weight of a solid element multiplied by its specific heat is almost the same for all elements, and approximately equal to 6.3. This is the number of calories required to raise the temperature of the atomic weight in grams of a solid element through 1° C., and is called the **atomic heat**. Thus, for solid elements :  $\text{atomic heat} = \text{atomic weight} \times \text{specific heat} = 6.3.$

The following table shows the relation :

Element.				Atomic weight	Specific heat	Atomic heat
				A.	C.	AC.
Copper	-	-	-	63.5	0.09	5.9
Iron	-	-	-	56	0.11	6.1
Lead	-	-	-	207	0.03	6.41
Iodine	-	-	-	127	0.0524	6.64
Mercury (solid)	-	-	-	200.6	0.033	6.7
Phosphorus (yellow)	-	-	-	31	0.198	5.2
Sulphur	-	-	-	32	0.175	5.6
Zinc	-	-	-	65.5	0.094	6.2

As Dulong and Petit expressed it, all atoms of solid elements have the same capacity for heat. Thus, if we determine the specific heat of a solid element and divide 6.3 by this specific heat, we obtain the *approximate* atomic weight. By comparing this with the exact equivalent found by chemical analysis, say of the chloride of the element, we find which multiple of the latter is equal to the *exact* atomic weight.

It must be noted that *certain elements of small atomic weight show deviations from Dulong and Petit's law*. Their atomic heats are *smaller* than 6.3, e.g., those of carbon (1.9), boron (2.6) and silicon (4.8). At high temperatures, however, these atomic heats tend to become normal, as is seen from the following table :

Element.				Temperature.	Atomic heat.
Carbon	-	-	-	980°	5.6
Boron	-	-	-	233°	4.3
Silicon	-	-	-	232°	5.68

At very low temperatures the atomic heats of *all* elements become small, and in some cases very small. In the case of the diamond the atomic heat has vanished at the very low temperature of liquid hydrogen. This is explained by Planck's quantum theory (p. 190).

It was found by experiments made by Joule that the **molecular** heat of a compound (= molecular weight  $\times$  specific heat) is *the sum of the atomic heats of its elements*. For example, the specific heat of lead iodide,  $\text{PbI}_2$ , is 0.0427. The molecular weight is  $207 + (2 \times 127) = 461$ , hence the molecular heat is  $461 \times 0.0427 = 19.68$ . The sum of the atomic heats is  $6.41 + (2 \times 6.64) = 19.69$ . The atoms preserve their atomic heats in combination.



As an example of the application of atomic heats to the determination of atomic weights, consider the case of tin. This forms with chlorine a volatile liquid, stannic chloride, the vapour density of which is found by experiment to be 132.9, hence the *approximate* molecular weight is  $132.9 \times 2 = 265.8$ . By *exact* analysis it is found that the compound contains in percentages: tin 45.6; chlorine 54.4. The amount of chlorine in 265.8 parts of stannic chloride is  $54.4 \times 265.8 \div 100 = 144.6$ . This, however, is approximately  $4 \times 35.5 = 142.0$ , and hence we may assume that the molecule of stannic chloride contains four atoms of chlorine, or the formula is  $\text{Sn}_x\text{Cl}_4$ . To find  $x$  we require additional information. Now, the specific heat of tin is 0.056, hence the *approximate atomic weight* of tin is  $6.3 \div 0.056 = 113$ . From the *exact* analysis of the compound, however, we find that the amount of tin combined with four atoms of chlorine is  $45.6 \times 142.0 \div 54.4 = 119$ . By comparison with 113, we conclude that 119 is the *exact atomic weight* of tin, so that stannic chloride contains one atom of tin ( $x = 1$ ) and its formula is  $\text{SnCl}_4$ .

(N.B.—The steps in this argument must be carefully followed and the *approximate* and *exact* values carefully distinguished. Failure to do this leads to frequent mistakes with beginners.)

\* **Crystals.**—Many solids exist in definite crystalline forms, which are different for different substances, as is seen from Fig. 136. The science of crystallography is concerned with the classification of these forms, and a practical division of crystals is that into six classes or systems, depending on the crystal axes, imaginary lines within the crystal, shown in Fig. 137. These systems are (1) the **regular** (three equal axes at right angles); (2) the **tetragonal** (two equal axes at right angles, and a third longer or shorter at right angles); (3) the **orthorhombic** (three unequal axes, all at right angles); (4) the **hexagonal** (three equal axes making angles of  $60^\circ$  with one another and another axis at right angles); (5) the **monoclinic** (three axes, all unequal, two of which are at right angles, and one of them is at right angles to the third); and (6) the **triclinic** (or *anorthic*) (three axes all unequal and inclined). A prism and pyramid form of each of the first four systems are shown.

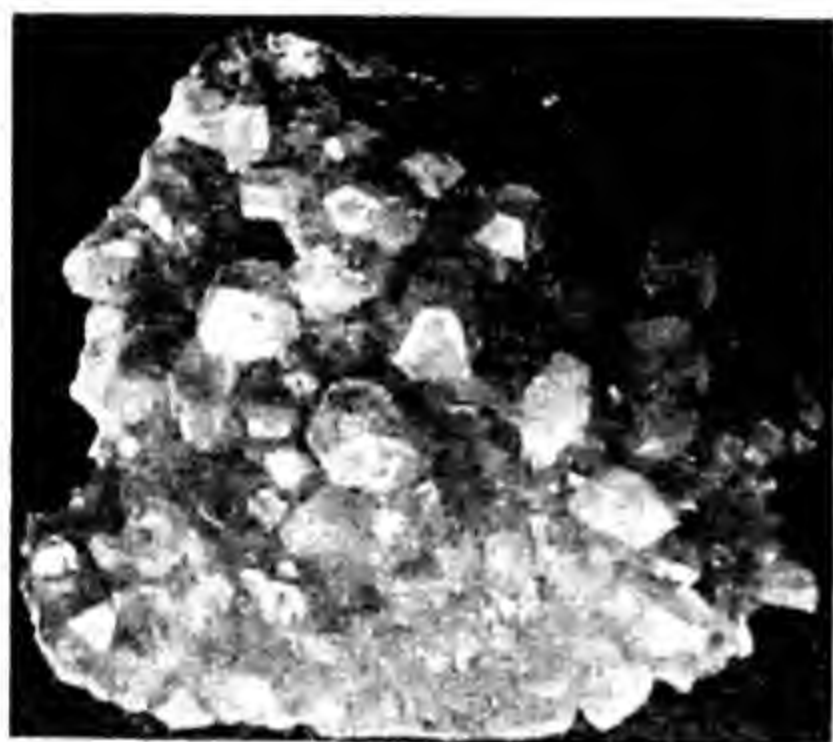
In a *gas* the molecules are widely separated and moving in straight lines. In a *liquid* the molecules are close together and attract one another, but they are still moving from place to place, as we know from the diffusion which takes place in liquids. If a liquid is cooled, the motion of the molecules becomes slower



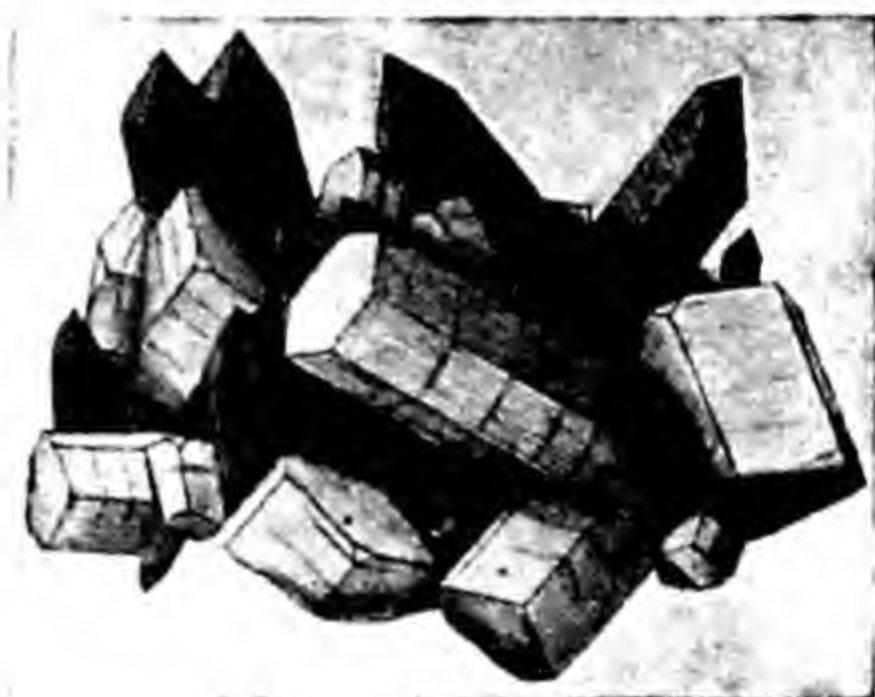
I. REGULAR.



II. TETRAGONAL.



III. CRYSTAL MASSES.



IV. HEXAGONAL.



V. MONOCLINIC.



VI. TRICLINIC.

FIG. 15. CRYSTAL FORMS AS SHOWN IN MINERALS.



and slower, and if we were to go on cooling the mass we could imagine that the molecules would become in the end practically immobile. They still exert large forces on one another, so that when we try to alter the shape of the mass a great resistance is

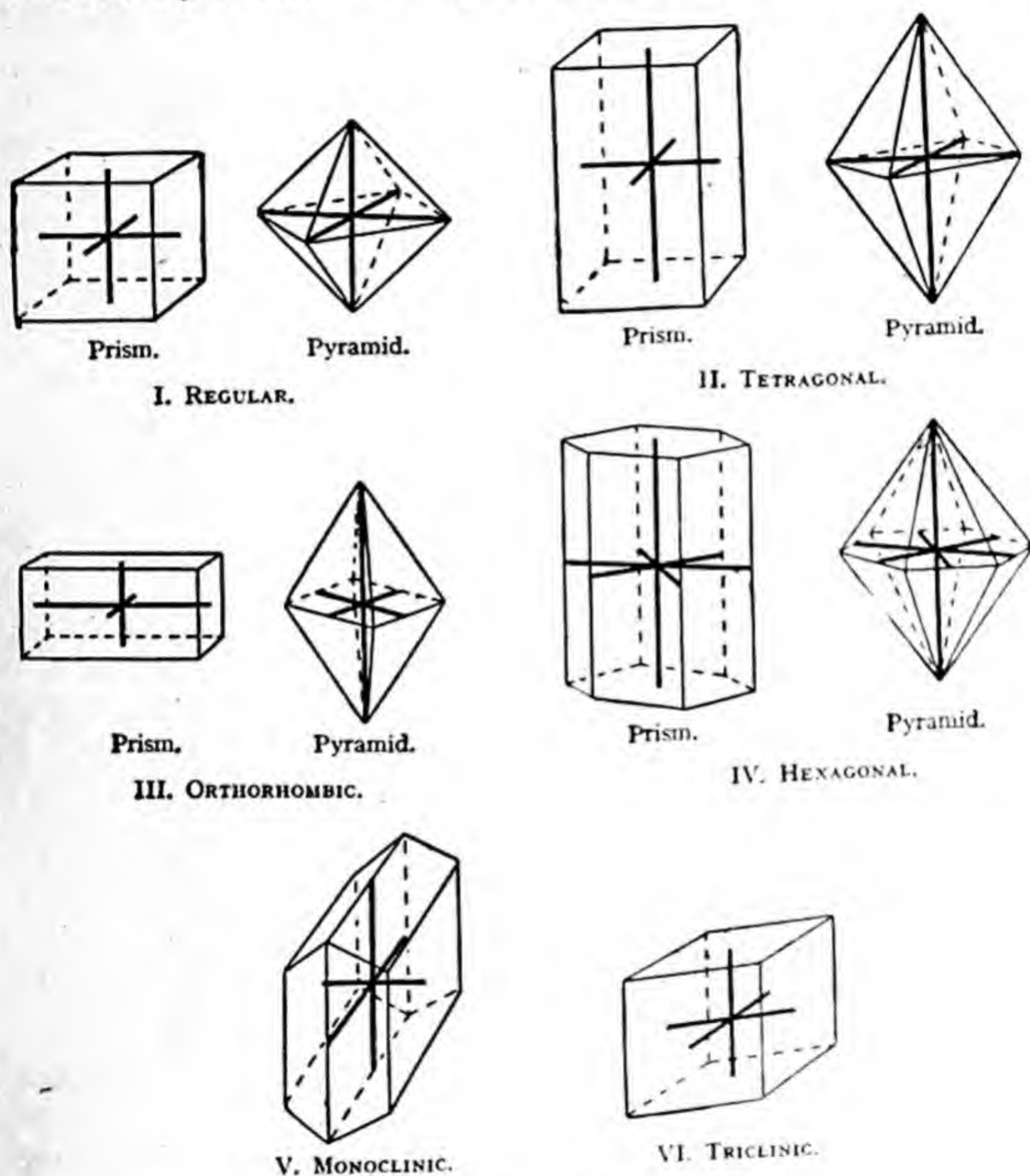


FIG. 137.—CRYSTAL SYSTEMS.

encountered; the whole has now become what would generally be described as a *solid*. The resistance to change of shape which is encountered in stirring such a liquid as treacle is called **viscosity**: when the liquid solidifies the viscosity has become very large. In a solid formed according to this picture the

molecules are arranged in a very haphazard fashion. There is nothing to distinguish the mass from a liquid except its great viscosity, and the type of solid so formed is like glass or barley sugar—it is in what is called the *vitreous* (glassy) *state*. **Vitreous** solids are amorphous, have no obvious crystalline form, and since



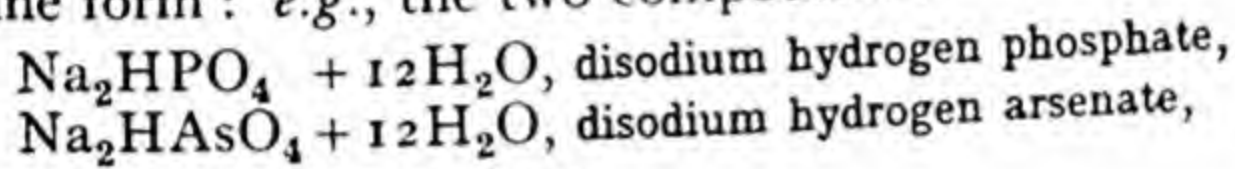
JOHN DOUGLASS (1764-1863)

as the liquid is exposed to a stress for a very long time, it is generally regarded as **supercooled** liquid. The term 'solids' is properly called 'solids' only when the particles are properly arranged in a true crystalline form. A piece of rock-salt or ice-cube is a true solid, which makes all the difference between the liquid and the solid. An amorphous solid is still a true solid, or



crystal, is like a brigade of infantry which has been halted in proper formation.

**Isomorphism.**—In 1819, the same year in which Dulong and Petit announced their law, Eilhard Mitscherlich, a student of Oriental philology who became interested in science and finally occupied the chair of chemistry at Berlin, published a fundamental memoir: 'On the relation which exists between the crystalline form and chemical proportions. First Memoir, on the identity of crystalline form among many different substances and on the relation of this form to the number of elementary atoms in the crystals.' He found that phosphates and arsenates, when they were of similar composition and contained the same amount of water of crystallisation, had almost exactly the same crystalline form: *e.g.*, the two compounds:



yield crystals of the same form.

The capacity of different, but chemically similar, substances of crystallising in the same form was called by Mitscherlich

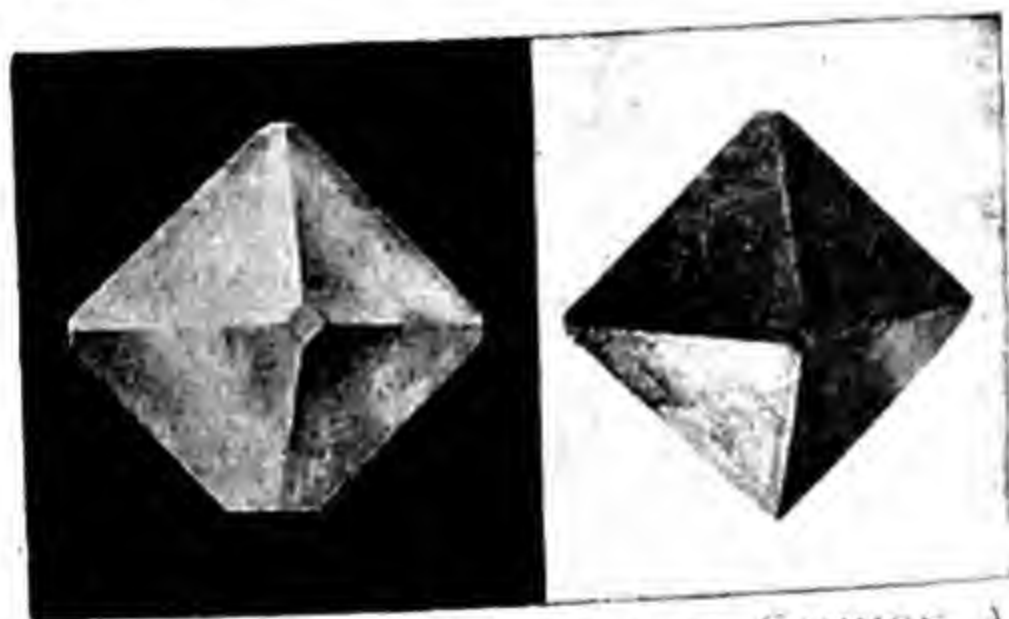


FIG. 139.—ISOMORPHOUS CRYSTALS OF COMMON ALUM AND CHROME ALUM (right).

**isomorphism**; substances crystallising in the same form are called **isomorphous**. Other examples of isomorphous substances are **common alum**,  $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$  and **chrome alum**,  $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$  (Fig. 139). Isomorphous elements are those which form similarly crystallising compounds with the same elements or radicals. It is not necessary that the *free* elements shall have similar crystalline forms, although this is sometimes the case.

An atom of one element may, therefore, be replaced in a molecule of a compound by an atom of an isomorphous element

without changing the crystalline form. An atom of arsenic, for instance, may be substituted for an atom of phosphorus in  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ , producing  $\text{Na}_2\text{HAsO}_4 + 12\text{H}_2\text{O}$ , and the second compound is isomorphous with the first.

The *formulae* of similar compounds may be deduced from their isomorphism: thus, from the fact that potassium selenate crystallises in the same form as potassium sulphate, Mitscherlich concluded that its formula must be  $\text{K}_2\text{SeO}_4$ , corresponding with  $\text{K}_2\text{SO}_4$ . From its composition the atomic weight of selenium could then be calculated.

Again, ferric oxide, chromic oxide, and aluminium oxide are isomorphous, since mineral crystals of these compounds have the same form. The vapour density of aluminium chloride and the atomic heat of aluminium correspond with the formula  $\text{AlCl}_3$ . The formula of the oxide will then be  $\text{Al}_2\text{O}_3$ . We therefore *assume* the formulae  $\text{Fe}_2\text{O}_3$  for ferric oxide and  $\text{Cr}_2\text{O}_3$  for chromic oxide, and from the percentage compositions of these oxides the atomic weights of the metals may be calculated. These are confirmed by the specific heats of the metals, which are 0.1096 and 0.104, respectively.

A very important property of isomorphous substances is their capacity of crystallising together from solutions so as to form *homogeneous* crystals containing the isomorphous substances in variable proportions. These crystals are usually known as **mixed crystals**; another name is **solid solutions**.

Thus, if chrome alum,  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , and ordinary potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , which form deep purple and colourless octahedral crystals, respectively, are dissolved together in water and the solution is allowed to crystallise, octahedral crystals containing both alums separate, having colours varying from a very pale purple to deep purple according to the amount of chrome alum they contain.



FIG. 140.—OVERGROWTH CRYSTAL.

Isomorphous compounds cannot, therefore, be separated in a state of purity by crystallisation, as is the case with salts of different chemical types, crystallising in different forms, such as potassium nitrate and sodium chloride (p. 41).



If an octahedral crystal of chrome alum is suspended by a thread in a saturated solution of potash alum, a colourless overgrowth of the latter salt is deposited on the violet crystal as nucleus. Similarly, a green crystal of nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , may be covered with a colourless crystal of magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Fig. 140). The property of forming such **layer crystals**, or **overgrowth crystals**, is shown by isomorphous substances.

Isomorphous substances therefore (1) crystallise in the same form; (2) form mixed crystals; (3) form overgrowth crystals.

\* **The structure of crystals.**—It has long been realised that the outward definite shapes of crystals correspond with some orderly internal arrangement of the atoms and molecules composing them. Just as the shape of a house depends on the careful

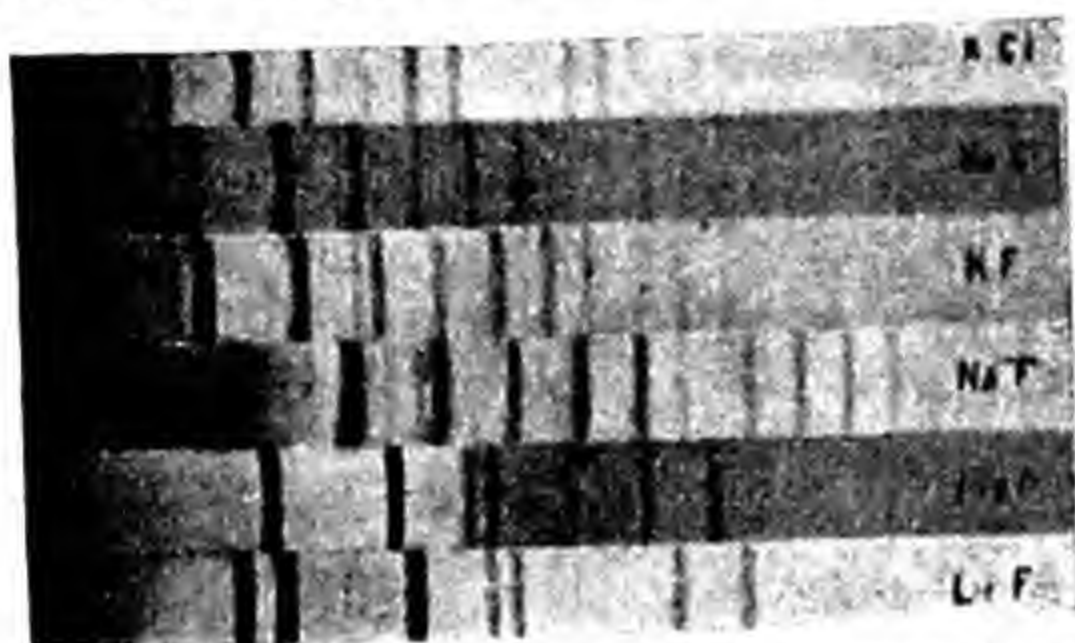


FIG. 141.—X-RAY SPECTRA OF VARIOUS SALTS.

arrangement of the bricks or blocks of stone from which it has been built according to some definite plan, so the shape of a crystal seems to depend on a particular and definite arrangement of the atoms or molecules which form its structural units. In recent years this interior structure of crystals has been explored by means of the X-rays.

The waves of ordinary light are too large to be seriously affected by the very small atoms in a crystal, and the light passes through the material of the crystal without suffering any scattering effect.

With X-rays, which are of wave-lengths not much longer than the diameters of atoms ( $10^{-8}$  cm.), the effect of the atoms is appreciable, and the rays are deviated by the separate atoms in the crystal, or even in a powdered crystal. The rays passing through, when allowed to fall on a photographic plate, form a definite pattern of lines or spots, corresponding with an **X-ray spectrum** (Fig. 141). From the nature of this spectrum, and

other simple information, it is possible, as Sir William Bragg and his son Prof. W. L. Bragg, and also Prof. P. Debye have shown,

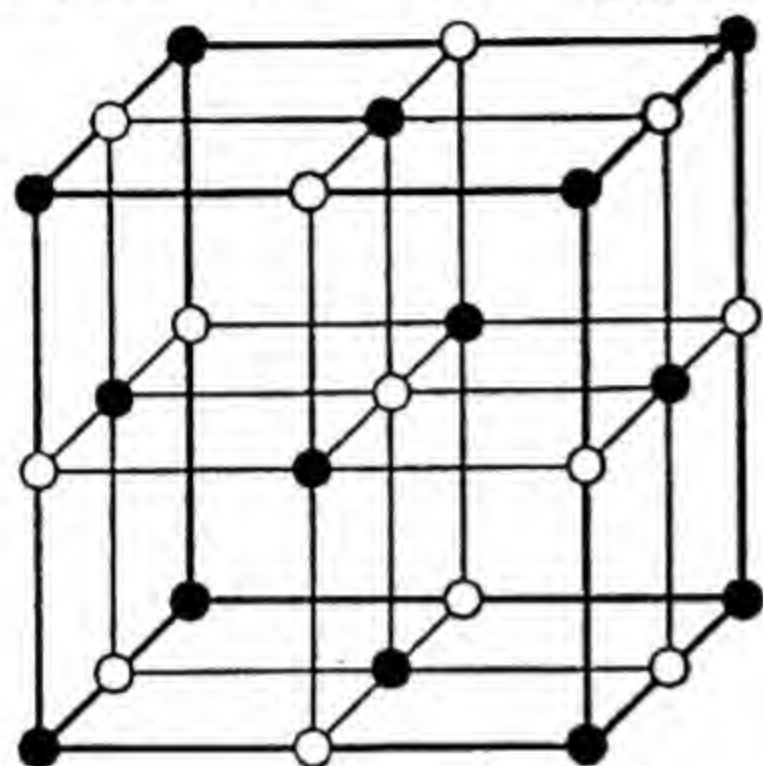


FIG. 142.—ARRANGEMENT OF THE ATOMS OF CHLORINE (black) AND ATOMS OF SODIUM (white) IN A SIMPLE CUBIC LATTICE OF ROCK-SALT.

atoms (ions) and the radical  $\text{CO}_3$  form the structural units. This method of X-ray crystal analysis has been extensively used and has thrown much light on the internal structure of solid compounds.

\* The quantum theory.—The particles of a crystal possess energy. The particles are constrained to the lattice points but perform small oscillations about them. The energy of the particle is like that of a vibrating spring or tuning fork, partly kinetic and partly potential, and one form is always changing over into the other. Each particle has a definite period of vibration, or frequency, just like a small tuning fork.

It is a remarkable result of modern research in physics that the energy of such a vibrating particle cannot increase or decrease continuously, but must

to calculate how the atoms in a crystal are arranged. They are built up into a lattice, or mass-produced pattern repeated over and over again; a kind of molecular sky-scraper framework, each little pattern being called a unit cell. Fig. 142 shows the lattice arrangement of rock-salt, the chlorine and sodium atoms being shown: really they are the chlorine and sodium *ions* (p. 201). There are no molecules of  $\text{NaCl}$  as such in the crystal, but only these atoms built up into a cubical lattice. Fig. 143 shows the lattice of Iceland spar: here the calcium

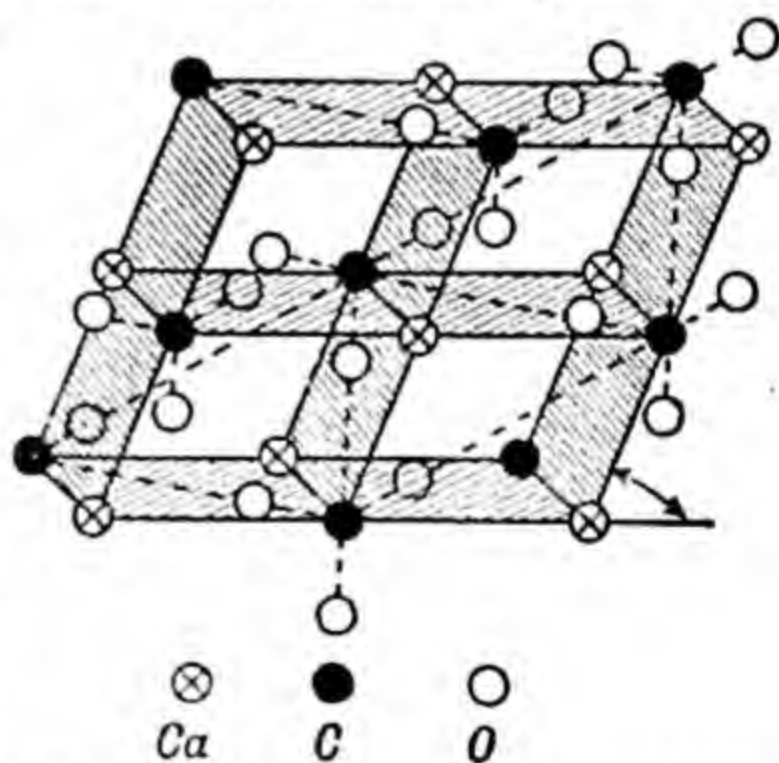


FIG. 143.—CRYSTAL STRUCTURE OF ICELAND SPAR.

EACH CARBON ATOM IS ASSOCIATED WITH THREE OXYGEN ATOMS ARRANGED SYMMETRICALLY AROUND IT, SO THAT THE CARBONATE RADICAL,  $\text{CO}_3$ , PRESERVES AN INDEPENDENT EXISTENCE IN THE CRYSTAL.



always do so in whole multiples of a quantum of energy, equal to the frequency of vibration multiplied by a constant,  $h$ , the same for all particles or other systems in which quantum distribution holds the field, and called **Planck's constant**, from the originator of the quantum theory, Max Planck, the great German physicist (Fig. 144).

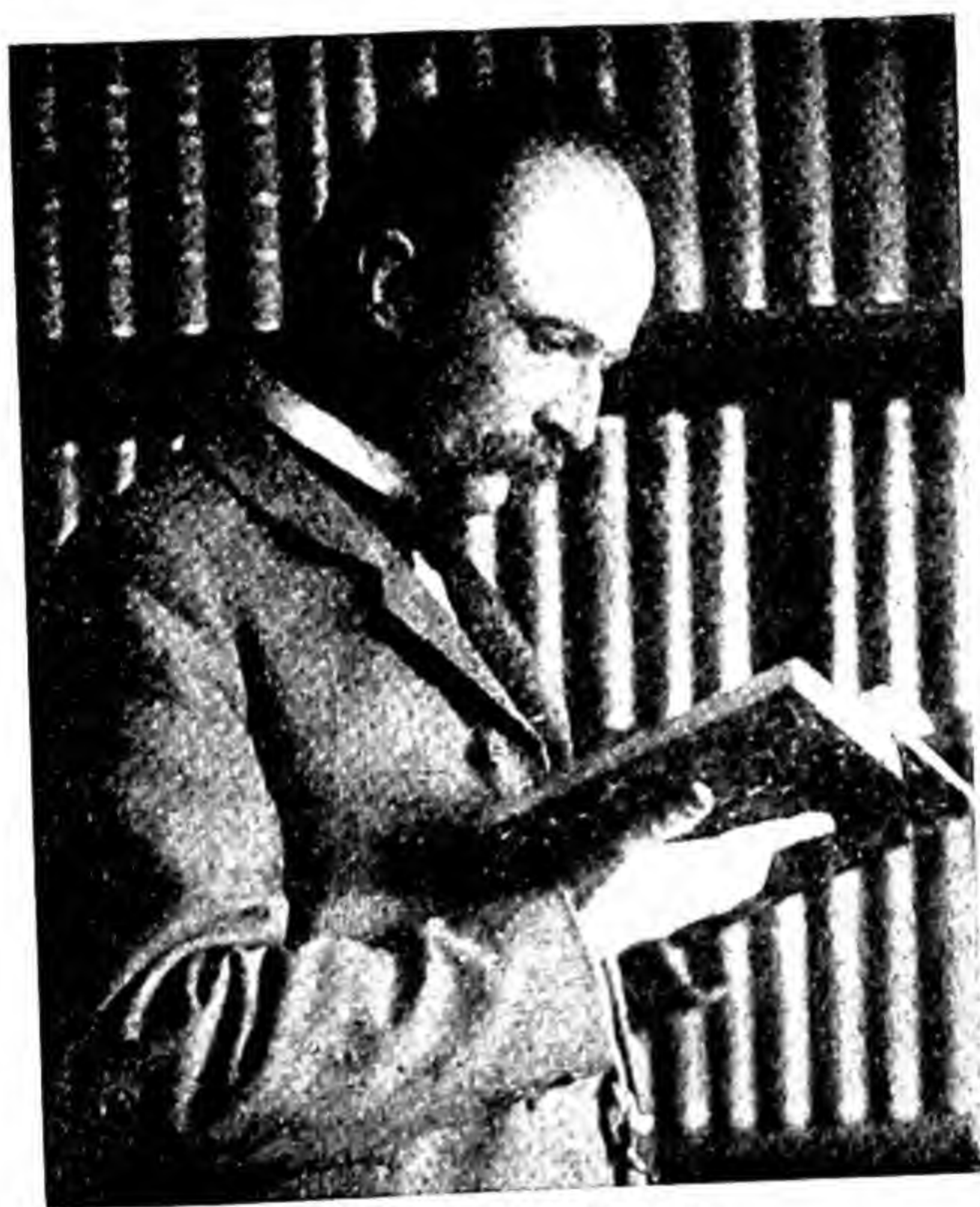


FIG. 144 MAX PLANCK.

Now imagine what will happen when the solid is cooled down. The particles will give out energy in quanta. When the particle is left with only one quantum it must, in the next step, give out *the whole* of its energy. The crystal will then be devoid of energy, although the temperature is still above the absolute zero. It is clear that the larger the quantum which is characteristic of a body the sooner this will happen. The diamond has

lost all its quanta even at the relatively high temperature of the boiling point of liquid hydrogen (p. 182). The elements with low atomic heats absorb energy only in multiples of *large* quanta, and hence at low temperatures their atoms find it difficult to provide themselves with energy. A bank which accepted deposits only in multiples of £1,000,000 would probably not have such a large capital as one which took in cash or cheques on the usual terms.

The conductivities of some metals for electricity also increase abnormally with fall in temperature, and at the temperature of liquid helium, about  $4^{\circ}$  absolute, the resistance of mercury, lead and tin has become so small that an electric current set up in a ring of the very cold metal by induction will go on circulating for hours once it is started. Other metals, such as platinum, gold, copper and iron, do not assume this *superconducting* state at very low temperatures.

When the atomic frequency is small, the quantum is small, and energy may be taken up or lost *almost* continuously. Dulong and Petit's law is then very nearly followed, even to low temperatures. This is the case with lead. At very low temperatures deviations become apparent even in these cases.

Atoms which are tightly bound will probably have high frequencies, just as the frequency of the note emitted by a stretched wire increases as the tension of the wire is raised. Thus, high frequencies may be expected in very hard solids, such as diamond.

**\* Cohesive forces.**—The considerations just advanced may throw some light on the nature of those obscure forces between the particles of matter which are called forces of *cohesion* (p. 185). It is cohesion which keeps the molecules of liquids from flying off to become a gas, and also marshals the constituent particles of a crystal lattice into the 'strait-waistcoats' of the unit cells. In a rock-salt crystal the sodium and chlorine particles, or ions, are oppositely charged with electricity, and it is known from Coulomb's law, if it holds at such small distances (it seems to hold even within the atom, between the positive nucleus and the planetary electrons), that these charges *attract* one another with a force varying inversely as the square of the distance between them. To hold them out at arm's length in the severe but beautiful pattern of the lattice there must also, apparently, be another force, of *repulsion*, and calculations based on the compressibility of crystals indicate that this repulsive force varies inversely as the ninth or some higher power of the distance.



These two forces hold each other in equilibrium. This is an old idea, due to Boscovich in the eighteenth century, but only recently worked out in detail by Born. It is doubtful if it conveys the whole story, and in some cases an attractive force not due to electrical charges has been assumed as well.

When a crystal is melted or dissolved the lattice fades away and 'leaves not a wrack behind.' The particles escape from the prison cells and move about at random. Sudden cooling may arrest this motion before the particles have had time to get back to their cells: an amorphous solid results. When this is heated for some time below the point of liquefaction the particles arrange themselves into a lattice, and this is probably the explanation of annealing.

## CHAPTER XII

### VALENCY

**Valency.**—Hydrogen compounds exist in which one atom of an element is combined with one, two, three, or four atoms of hydrogen :

$\text{HCl}$	$\text{H}_2\text{O}$	$\text{H}_3\text{N}$	$\text{H}_4\text{C}$
Hydrochloric acid.	Water.	Ammonia.	Methane.

The atoms of chlorine, oxygen, nitrogen, and carbon are capable of uniting with one, two, three, and four atoms of hydrogen, respectively. None of these compounds of hydrogen contains more than one atom of an element combined with one atom of hydrogen, and the latter is therefore taken as the standard of combining capacity or valency. The valency of an element is measured by the number of hydrogen atoms which unite with one atom of that element. The above examples show that chlorine, oxygen, nitrogen, and carbon are **univalent**, **bivalent**, **tervalent**, and **quadrivalent** respectively.

Since chlorine is univalent, it may be used instead of hydrogen in determining the valencies of elements ; the valencies thus found are the same as those referred to hydrogen, but **quinquevalent** and **sexivalent** elements are now included :

$\text{Cl}_2\text{O}$	$\text{Cl}_3\text{N}$	$\text{Cl}_4\text{C}$	$\text{Cl}_5\text{P}$	$\text{Cl}_6\text{W}$
Chlorine monoxide.	Nitrogen trichloride.	Carbon tetrachloride.	Phosphorus pentachloride.	Tungsten hexachloride.

Oxygen is bivalent, and if it combines with one atom of another element the latter (*e.g.*, calcium in calcium oxide,  $\text{CaO}$ ) is also bivalent and will combine with two atoms of hydrogen



( $\text{CaH}_2$ ) or chlorine ( $\text{CaCl}_2$ ). In oxygen compounds two additional valencies appear, 7 and 8, the latter being the highest valency known :

$\text{Na}_2\text{O}$ Sodium monoxide.	$\text{CaO}$ Calcium oxide.	$\text{Al}_2\text{O}_3$ Aluminium oxide.	$\text{CO}_2$ Carbon dioxide.
$\text{P}_2\text{O}_5$ Phosphorus pentoxide.	$\text{SO}_3$ Sulphur trioxide.	$\text{Cl}_2\text{O}_7$ Chlorine heptoxide.	$\text{OsO}_4$ Osmium tetroxide.

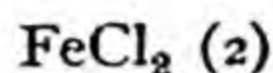
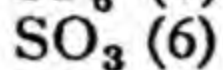
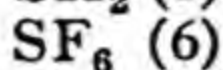
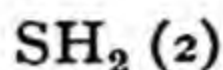
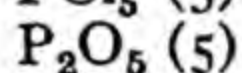
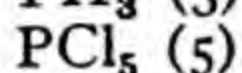
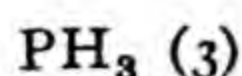


FIG. 145.—EDWARD FRANKLAND, 1825-1897.

Chlorine is **septavalent**, and osmium is **octovalent**, in their highest oxides. An octofluoride of osmium,  $\text{OsF}_8$ , is also known.

The inactive gases argon, helium, etc., form no compounds with any elements, and their valency is zero. We have therefore, in all, eight valencies shown by various elements, viz., 1, 2, 3, 4, 5, 6, 7, and 8.

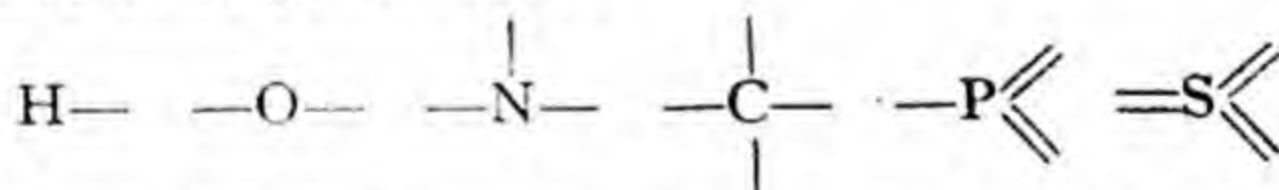
An element may show different valencies in its compounds, e.g. phosphorus may have valencies of 3 and 5, sulphur may have valencies of 2 and 6, iron may have valencies of 2 and 3, etc.



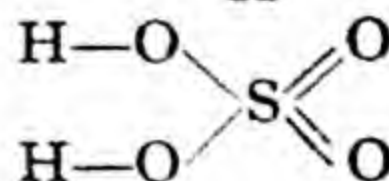
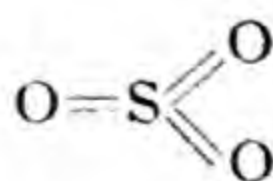
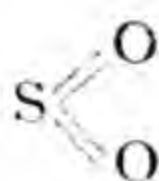
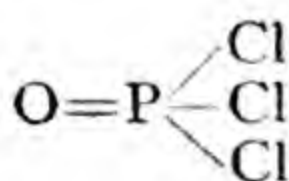
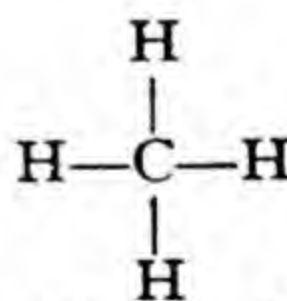
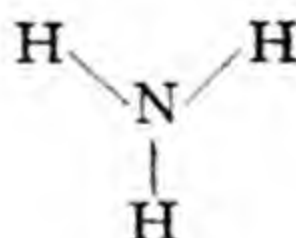
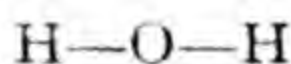
The *equivalent* is the weight of an element which combines with or displaces unit weight (one atom) of hydrogen. The *valency* is the number of unit weights (atoms) of hydrogen which combine with one atomic weight of an element. Hence :

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent}}.$$

**Structural formulae.**—The linking of atoms together to form compounds may be pictured by assuming that each atom has a number of bonds equal to its valency. These valency bonds are shown by lines drawn from the symbol of the atom, the number of bonds corresponding with the valency. Thus, hydrogen has one bond, oxygen has two bonds, phosphorus has three or five bonds, and so on :

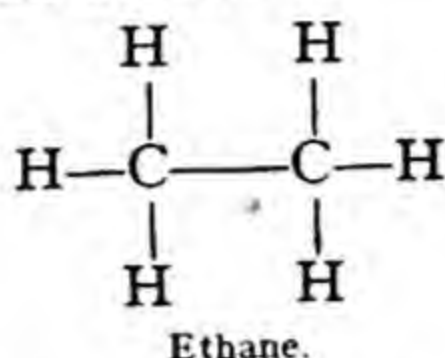


When atoms link together, a bond of one atom joins with a bond of another atom to form a single bond, shown by one line, and no free bonds must be left over :





Multivalent atoms can sometimes link with each other by using one or more bonds on each atom, the remaining bonds being free to attach other atoms :

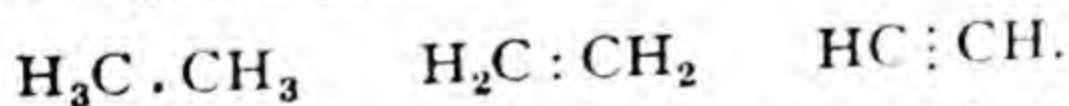


Such formulae as we have just been using are called **structural formulae** ; they are supposed to represent the way in which the atoms are united in the molecules. Modern organic chemistry, or the chemistry of carbon compounds, is almost exclusively concerned with the determination of the structure of molecules, and the behaviour of a carbon compound is generally understood more or less accurately when its structural formula is known.

**Saturated and unsaturated compounds.**—In some cases it is assumed that *two* or more valencies of an atom of an element can link with a corresponding number of valencies of an atom of the *same* element :

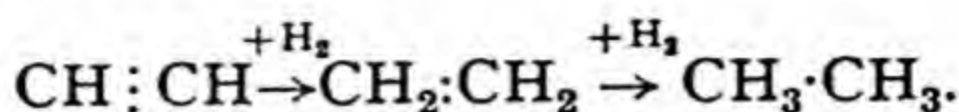
1. **Ethane,** 
$$\begin{array}{c}
 \text{H} \quad \text{H} \\
 | \quad | \\
 \text{H}-\text{C}-\text{C}-\text{H} \\
 | \quad | \\
 \text{H} \quad \text{H}
 \end{array}$$
single bond, or linkage, between carbon atoms.
2. **Ethylene,** 
$$\begin{array}{c}
 \text{H} \quad \text{H} \\
 | \quad | \\
 \text{C}=\text{C} \\
 | \quad | \\
 \text{H} \quad \text{H}
 \end{array}$$
double bond, or linkage, between carbon atoms.
3. **Acetylene,** 
$$\text{H}-\text{C}\equiv\text{C}-\text{H}$$
triple bond, or linkage, between carbon atoms.

Such double and triple bonds are often represented by dots, to save space in printing, thus :

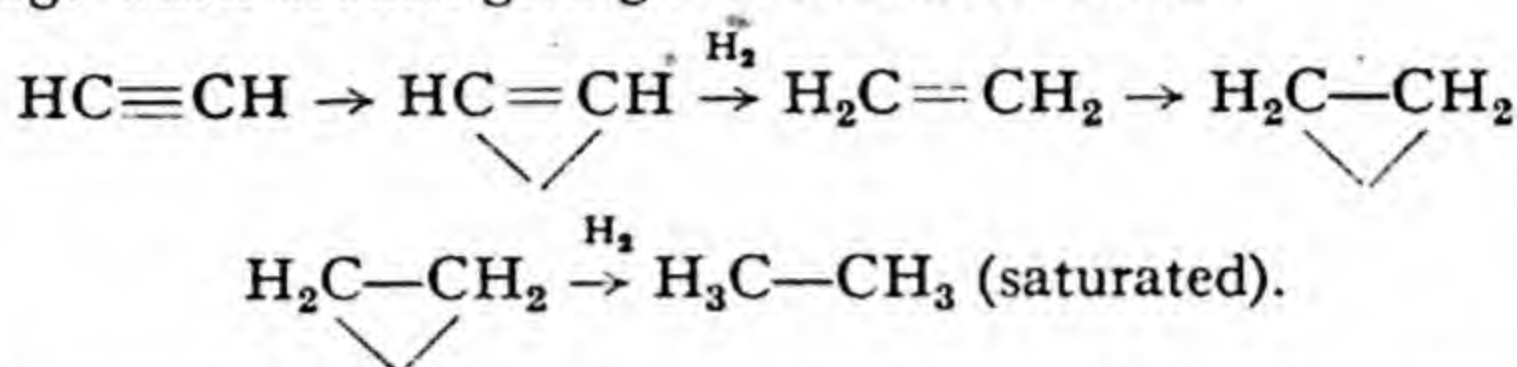


The propriety of this mode of representation is shown by the fact that the molecules of compounds with multiple bonds are

unsaturated, *i.e.*, they can add on other atoms to form saturated compounds :



The multiple linkages therefore contain latent bonds, each linkage when broken giving *two* available bonds :

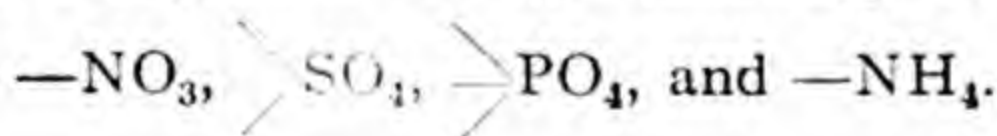


**Valency of radicals.**—The conception of valency may be applied not only to the atoms of the elements, but also to the radicals, or groups of atoms which take part as a whole in chemical reactions. Thus, in the hydrocarbons ethane, ethylene, and acetylene, we recognise the uni-, bi-, and ter-valent radicals  $-\text{CH}_3$  (methyl),  $\diagup\text{CH}_2$  (methylene), and  $\diagup\text{CH}$ , respectively.

In the same way an inspection of the table :

$\text{HNO}_3$	$\text{H}_2\text{SO}_4$	$\text{H}_3\text{PO}_4$	$\text{Na}_3\text{PO}_4$
$\text{NaNO}_3$	$\text{K}_2\text{SO}_4$	$\text{NaH}_2\text{PO}_4$	$\text{NaNH}_4\text{HPO}_4$
$\text{NH}_4\text{NO}_3$	$(\text{NH}_4)_2\text{SO}_4$	$\text{Na}_2\text{HPO}_4$	$(\text{NH}_4)_3\text{PO}_4$

leads to the recognition of the following radicals in the compounds :



(A *molecule* of a compound, or even of an element, such as  $\text{O}_2$ , has no valency.)

If we know the valencies of the elements and of common radicals, we can at once write down the formulae of all the salts formed from them.

It is usually most convenient to remember the formulae of a few typical compounds, from these to deduce the valencies of the elements or radicals, and thence to write down the formula of the compound required.

Thus, if we wish to write down the formula of aluminium sulphate, we remember the formulae  $\text{AlCl}_3$  and  $\text{H}_2\text{SO}_4$ . Hence we find that Al is trivalent and  $\text{SO}_4$  bivalent :  $-\text{Al} <, >\text{SO}_4$ . In order to satisfy the valencies of Al by those of  $\text{SO}_4$ , we shall have to take  $2\text{Al}$ , *i.e.*, 6 valencies, and  $3\text{SO}_4$ , also 6 valencies.



No free valencies must be left over. Hence aluminium sulphate is  $\text{Al}_2(\text{SO}_4)_3$ .

Saturated molecules often have the capacity of uniting with each other, although they cannot take up additional *atoms* of elements. Thus, hydrofluoric acid, HF, and potassium fluoride, KF, although both are saturated compounds, combine to form the salt potassium hydrogen fluoride,  $\text{KHF}_2$ . This salt is readily broken up on heating, into KF and HF, and it is usually called a molecular compound.

The following may perhaps be adopted as a formal definition of valency :

The valency of an atom or radical is measured by the number of atoms of hydrogen or its equivalent which can combine with or be displaced by one atom of the element or one molecule of the radical.

## CHAPTER XIII

### ELECTROLYSIS. THE THEORY OF IONS

**Electroplating.**—The tendency of metals to rust or become corroded on exposure to the atmosphere is often prevented by covering them with a thin layer of some metal which is not easily

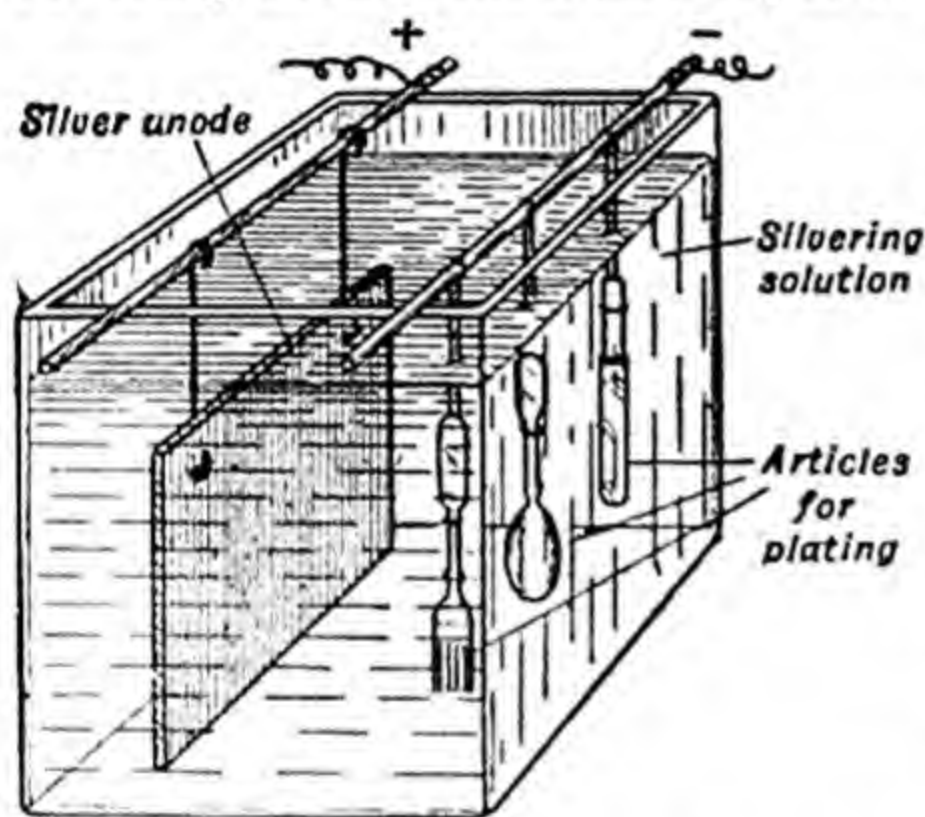


FIG. 146.—APPARATUS FOR ELECTROPLATING WITH SILVER.

attacked by air or moisture but which is too expensive to use alone. Silver plating, and nickel plating, are common examples, and more recently plating with chromium has been introduced. The second metal is nearly always deposited by means of electricity, and hence it is said that the first metal is **electroplated** with the second. Copper is electroplated with silver, and iron or brass with nickel. Not only is the process used in plating one metal with

another, but also for the purification of metals such as copper, and for the deposition of alloys such as brass. The simplest arrangement for electroplating is shown in Fig. 146. The object to be plated, say a spoon, is connected with the negative pole of a battery or dynamo, and a plate of silver is connected with the positive pole. The two are dipped into a solution of a silver salt. The silver dissolves from the plate and is deposited on the spoon. In reality the silver is deposited from the silver salt in the solution and at the same time more silver dissolves from the silver plate to replace that deposited from the solution.

**Electrolysis.**—When an electric current is passed through



acidulated water, decomposition occurs and hydrogen and oxygen gases are produced (p. 110). The process is called **electrolysis**, the acidulated water is called an **electrolyte**, and the platinum plates bringing the current into and out of the solution are called **electrodes**, the one connected with the positive pole of the battery being the **anode** and that connected with the negative the **cathode**. The current is carried through the solution by atoms or radicals of the electrolyte, that deposited on the anode being the **anion** and that deposited on the cathode the **cation**. Since unlike charges attract, the charge on the anion (attracted to the positive anode) will be negative, that on the cation positive. These names are summarised in the diagram in Fig. 147.

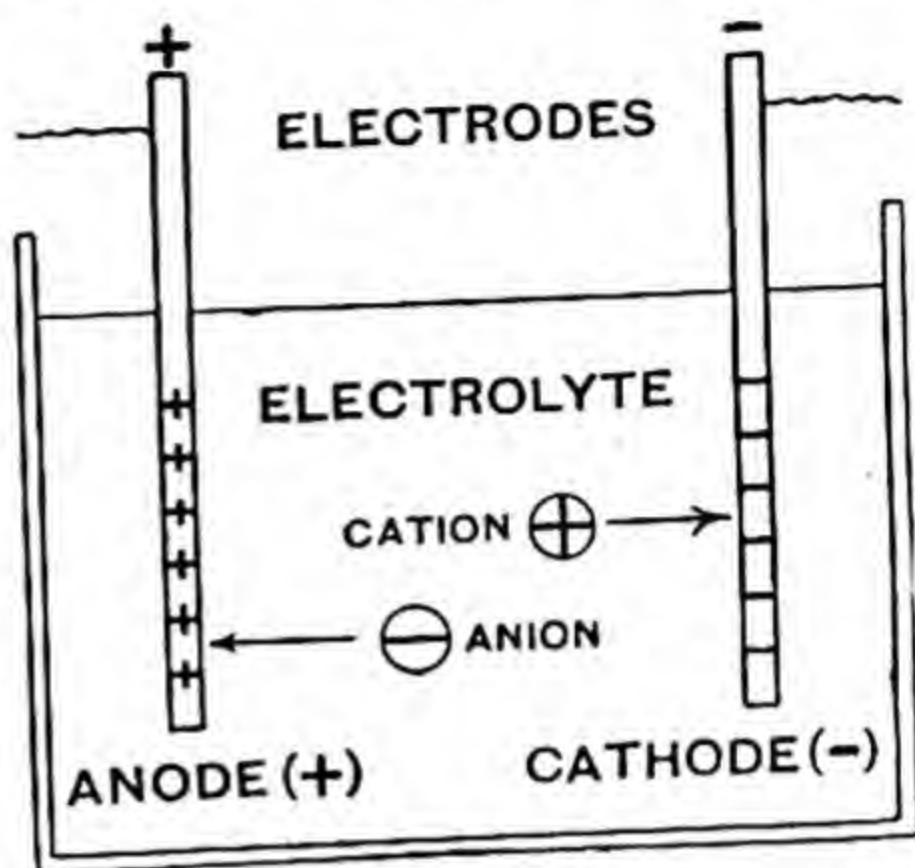


FIG. 147.—NOMENCLATURE OF ELECTROLYSIS.

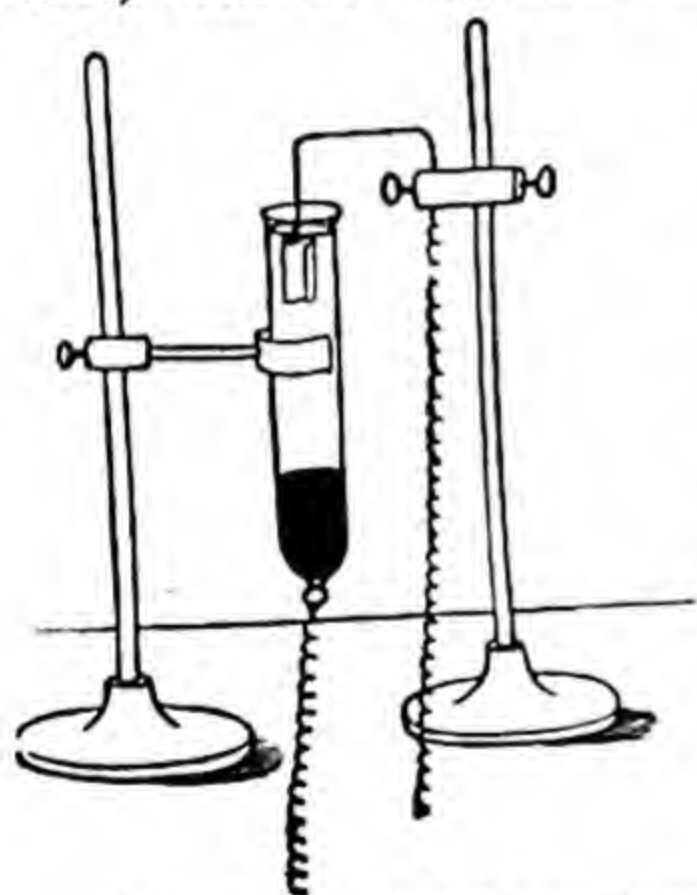
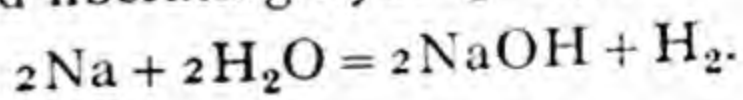


FIG. 148.—ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION WITH MERCURY AS THE NEGATIVE POLE.

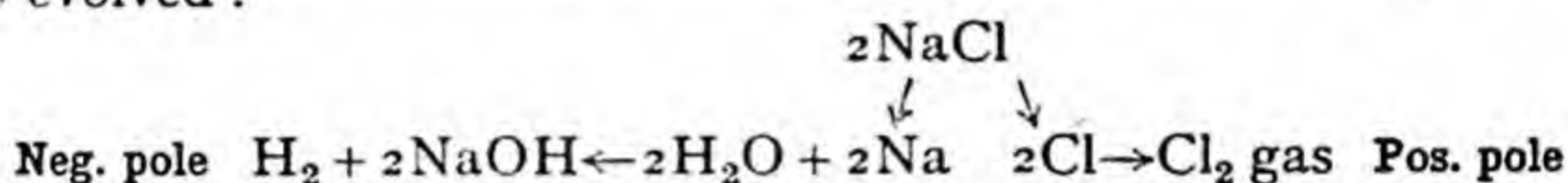
Concentrated hydrochloric acid is decomposed by electrolysis into hydrogen, deposited at the cathode, and chlorine, deposited at the anode. Fused sodium chloride is decomposed into metallic sodium, deposited on the cathode, and chlorine gas, deposited on the anode. With a *solution* of sodium chloride the sodium first deposited on the cathode at once reacts with the water, producing a solution of sodium hydroxide (caustic soda) and liberating hydrogen gas :



Chlorine is again evolved at the anode. If red litmus solution is added, it is turned blue around the cathode, owing to the alkali, caustic soda, produced, but it is

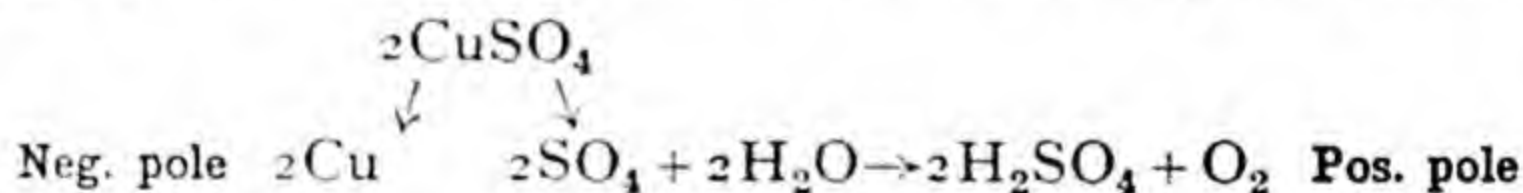
bleached around the anode by the chlorine liberated. The primary deposition of sodium at the cathode may be demonstrated by making the cathode consist of mercury, connected with the negative platinum wire (Fig. 148), when sodium amalgam will be formed and very little hydrogen evolved.

The effect of passing the current through a solution of sodium chloride is to cause the deposition of sodium and chlorine at the negative and positive poles respectively. The atoms of chlorine combine to form molecules of chlorine gas, which is evolved. The atoms of sodium at once react with the water present, forming caustic soda and liberating hydrogen, which is evolved :

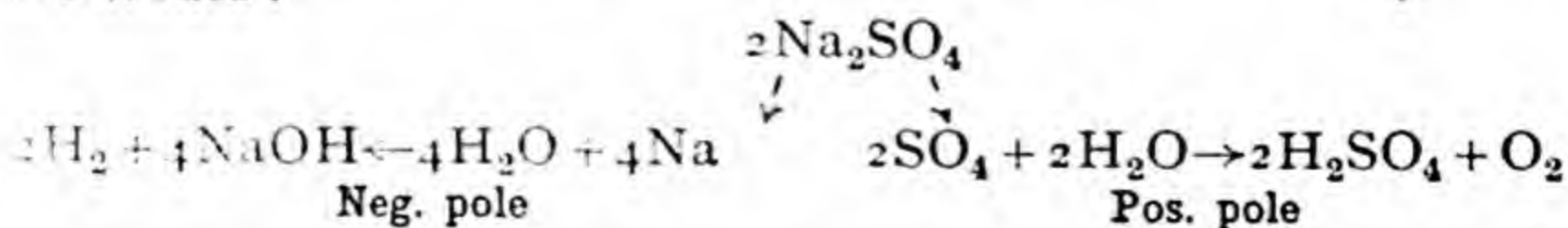


The *primary products* of the electrolysis are sodium and chlorine ; the sodium reacts with the water to give hydrogen and caustic soda, which are *secondary products*.

When a solution of copper sulphate is decomposed by a current there is a deposit of red metallic copper on the negative plate or pole (cathode), but no gas. At the positive pole (anode), sulphuric acid accumulates and a gas, oxygen, is evolved. In this case, also, a secondary reaction occurs. The  $\text{CuSO}_4$  is decomposed into Cu, which is deposited as metallic copper as a primary product on the cathode, and the  $\text{SO}_4$  radical is deposited on the anode. Here the  $\text{SO}_4$  at once reacts with water to form oxygen, which is evolved, and a solution of sulphuric acid :



A solution of sodium sulphate, on electrolysis, gives caustic soda and hydrogen gas at the cathode, and sulphuric acid and oxygen gas at the anode. Secondary actions now occur at both electrodes :



The production of acid and alkali may be exhibited by adding purple litmus to the solution of sodium sulphate and electrolysing



in a U-tube with platinum electrodes (Fig. 149). The litmus is turned blue by the alkali at the cathode and red by the acid at the anode. The hydrogen and oxygen gases evolved may be allowed to pass through side-tubes, collected and tested.

**Faraday's laws of electrolysis.**—The first systematic investigations of electrolysis were carried out by Humphry Davy and were continued by his pupil and assistant, Faraday. In 1832-33 the latter discovered two important laws of electrolysis.

Faraday connected in series a number of cells, containing different electrolytes, with a battery and an instrument for measuring the current (Fig. 150). Suppose, for example, that the first cell contains water acidulated with sulphuric acid, the second a solution of copper sulphate, and the third fused stannous chloride (tin dichloride,  $\text{SnCl}_2$ ).

After the current has passed for a certain time, the volumes of hydrogen and oxygen liberated from the acidulated water, and the weights of copper and tin deposited from the solution of copper sulphate and the fused stannous chloride, respectively,

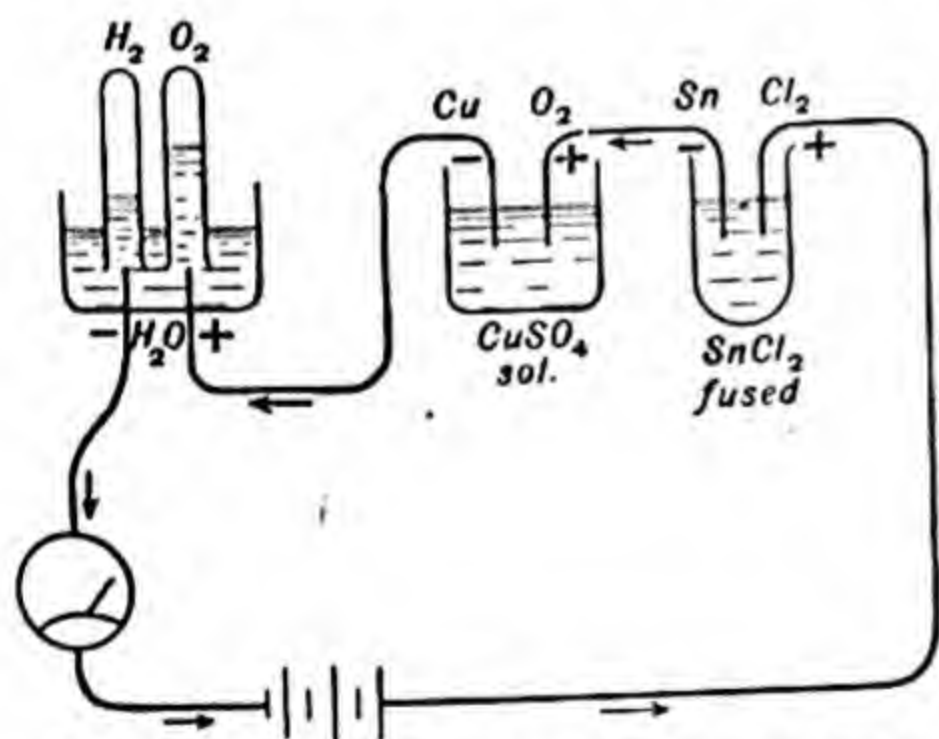


FIG. 150.—DIAGRAM OF ELECTROLYTIC CIRCUIT.

will be found that 96,500 coulombs of electricity have passed through the cells. Thus, 96,500 coulombs liberate 1 gm. of hydrogen. If this quantity of electricity passes as a small current for a long time (e.g., 0.1 ampere for 965,000 sec.) or as

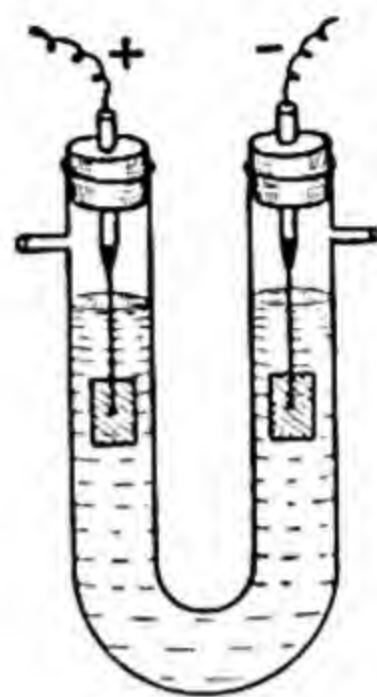


FIG. 149.  
ELECTROLYSIS OF  
SODIUM SULPHATE  
SOLUTION.

can be ascertained. The quantity of electricity which has passed through the solution is measured by the current strength multiplied by the time. The current strength is measured in amperes, and one ampere passing for one second corresponds with unit quantity of electricity, or one coulomb.

If the current passes until 1 gm. of hydrogen has been liberated from the acidulated water, it

a large current for a shorter time (e.g., 10 amperes for 9,650 sec.) the result is the same. Hence the weight of an ion deposited is proportional to the quantity of electricity which passes. This is Faraday's First Law of Electrolysis.

If the weights of the other ions which are deposited in the cells whilst 1 gm. of hydrogen is liberated in the first are determined, it is found that they are equivalent weights: 8 gm. of oxygen, 35.5 gm. of chlorine, 31.5 gm. of copper and 59 gm. of tin. Thus the weights of the different ions liberated by the same quantity of electricity are proportional to their chemical equivalents. This is Faraday's Second Law of Electrolysis, more concisely expressed in the form that 96,500 coulombs liberate one gram-equivalent of any ion in electrolysis.

Faraday's second law provides an obvious method of finding the equivalent of an element: for example, the equivalents of copper and tin could be determined in the experiment described.

**The theory of electrolysis.**—Since the ions are attracted by the electrodes, it is simplest to assume that they are themselves

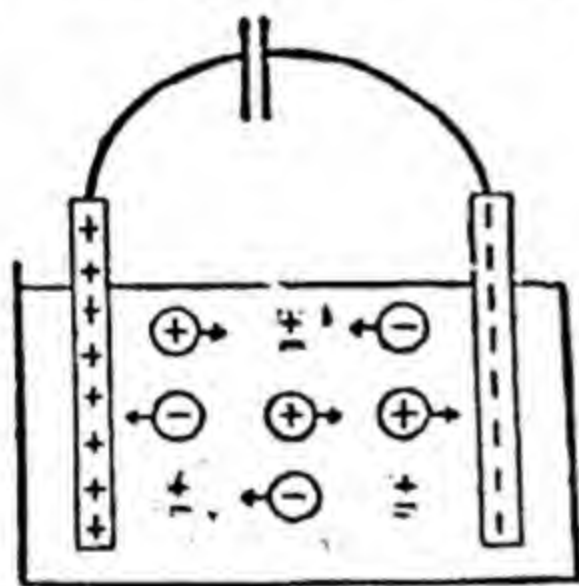


FIG. 151.—MIGRATION OF IONS IN ELECTROLYSIS.

charged, the sign of the charge on an ion being *opposite* to that of the electrode towards which it moves. Thus, anions are negatively charged atoms or radicals; cations are positively charged atoms or radicals. In the electrolyte we may picture two streams of charged ions moving in opposite directions to the two electrodes (Fig. 151), and these constitute the current in the electrolyte; the electricity is ferried across from one electrode to the

other by the charged ions, and this current completes that passing through the metallic circuit outside the cell. *The strength of the current is uniform throughout the whole circuit*, whether the latter is all metallic, or composed of metal wires and electrolytes. Since the current in the electrolyte is composed solely of charged ions, the weight of the latter moving to the electrodes in a given time is proportional to the current strength. This is Faraday's First Law.

Faraday's Second Law is simply explained by the assumption that the quantity of electricity associated with an ion is the same for all ions of the same valency, and is proportional to the valency. Thus, a univalent cation such as sodium carries one unit charge of positive electricity, a bivalent cation such as copper carries

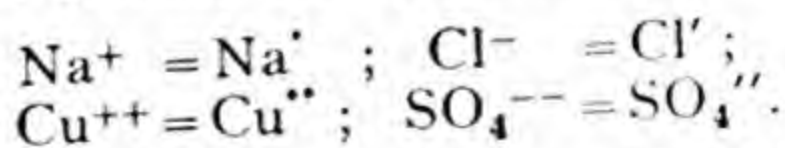


two unit charges of positive electricity, and so on. A univalent anion, such as chlorine, carries one unit charge of negative electricity, which is equal in magnitude but opposite in sign to the charge on the univalent cations, whilst a bivalent anion such as the sulphuric acid radical,  $\text{SO}_4$ , carries two unit negative charges, and so on.

The ionic charges carry with them the matter with which they are associated. When the ions reach the electrodes, the charges leave them, and the matter is deposited. Since the current is uniform throughout the circuit, the quantities of the ions deposited must all be proportional to the amounts associated with the same quantity of electricity. According to the theory advanced above, these amounts are in the proportion of the chemical equivalents. Thus, the same current deposits amounts of the ions which are proportional to the chemical equivalents. This is Faraday's Second Law of Electrolysis.

**The electron.**—The unvarying electric charge on univalent ions, and the simple multiple relation between the charges on multivalent ions, suggest at once that electricity, like matter, is divided up into atoms. This was suggested by Maxwell in 1873, with some reserve, and in 1874 G. J. Stoney made an approximate calculation of the magnitude of this unit electrical charge, which he called an electron. The electron theory was adopted by Helmholtz in 1881: 'The most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also is divided into definite elementary portions, which behave like atoms of electricity.' The free atom of electricity is the *negative* electron: unit negative charge is associated with an atom which has gained one electron, unit positive charge with an atom which has lost one electron. The hydrogen atom which has lost one electron is the positively charged mass known as the **proton**. The electron has a mass only about  $1/1845$  that of the hydrogen atom or of the proton.

For convenience, the charge of an ion is often represented by dots or dashes; one dot denotes unit positive charge, one dash unit negative charge:



**Theory of electrolytic dissociation.**—All experiments on electrolysis can be explained by the simple assumption that the ions move independently in electrolysis. They behave as if they were

free, and each ion responds to the attraction of the electrodes as if the other ions were not present. If the current is switched off, no visible change occurs in the solution, so that we may assume that the ions still remain free and independent of each other in the solution.



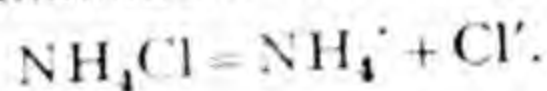
FIG. 15.—SVANTE ARRHENIUS (1859-1927).

Charnius (1857) assumed that in the solution of an electrolyte the molecules of the salt are broken up into ions, but the Swedish chemist Arrhenius first made the bold assumption, in 1887, that *every* free molecule of a salt, acid, or base in dilute solution are usually dissociated into ions of opposite charges moving free in solution and moving towards the electrodes during electrolysis. The current moves with the ions: in solution the current is the moving ions. When the ions reach the electrodes their charges are neutralised, and the uncharged atoms



or molecules are deposited. Thus, sodium chloride, when it is dissolved in water, is ionised into the sodium ion and the chloride ion:  $\text{NaCl} = \text{Na}^+ + \text{Cl}^-$ . In electrolysis, the negative chloride ions are attracted to the positive anode, and on reaching it each gives up an electron ( $e$ ), becoming a chlorine atom:  $\text{Cl}^- = \text{Cl} + e$ . These cannot exist as such, but combine in pairs to form chlorine molecules, which escape as chlorine gas. The positive sodium ions, on reaching the cathode, take from it negative charges, or electrons (which pass round the metallic circuit from the discharged chloride ions) and so become neutral sodium atoms:  $\text{Na}^+ + e = \text{Na}$ . These may dissolve in mercury, if the cathode is metallic mercury, or react with water, forming caustic soda and hydrogen, if the electrode is of platinum.

The ionisation of a dissolved electrolyte is entirely different from the thermal dissociation of a gas. Thus, ammonium chloride on heating dissociates into ammonia and hydrochloric acid:  $\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$ , but in solution it is electrolytically dissociated into the ammonium and chloride ions:



Since a solution of an electrolyte has no charge as a whole, the algebraic sum of the charges on the cations and anions must be zero.

Arrhenius's theory seemed doubtful to many chemists when it was put forward, but the whole of modern research both in physics and chemistry has only made it more and more probable. It stands second only to Dalton's atomic theory in the structure of modern chemistry.

**Migration of the ions.**—The bodily transfer of the ions under the influence of an electric field can be demonstrated by the apparatus shown in Fig. 153.

The U-tube is half-filled with a weak solution of potassium nitrate. By connecting a funnel with the capillary tap below the U-tube, a solution containing potassium permanganate is slowly admitted. The surface of separation between the colourless liquid above and the purple permanganate solution below should be quite sharp. A current is now passed between the platinum electrodes. The purple

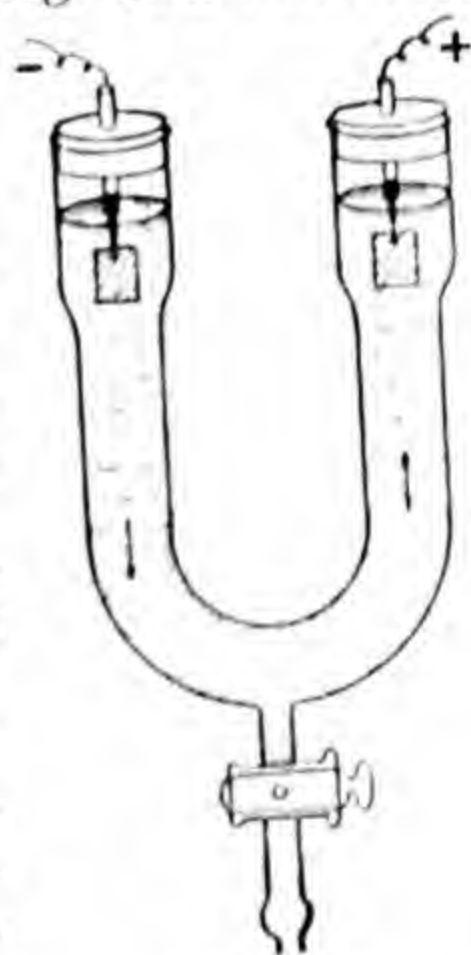


FIG. 153.  
DEMONSTRATION OF  
IONIC MIGRATION.

$\text{MnO}_4^-$ -ions at once begin to move towards the anode, and the levels alter in the directions shown (Fig. 153). If the former levels are marked by thin strips of gummed label, the change is quite apparent after 10-15 minutes.

It appears from this experiment that the actual speed of movement of the ions in bulk through the solution is very slow. They experience a great resistance, and it has been calculated that the force required to propel 1 mol of potassium ions through a solution with a speed of 1 cm. per sec. would amount to one and a half million tons.

**\* Abnormal freezing point depression of electrolytes.**—It has been stated on p. 175 that 1 mol of a non-electrolyte dissolved in 1000 gm. of water lowers the freezing point by  $1.86^\circ$ . The value for an electrolyte such as sodium chloride, dissociating into two ions, is  $3.72^\circ$ , *i.e.*, double the value for a non-electrolyte. This can be explained as due to the dissociation of the NaCl into two ions:  $\text{NaCl} = \text{Na}^+ + \text{Cl}^-$ , each of which acts as a separate molecule in producing a freezing point lowering, so that the depression is twice that which would be produced by a solute the molecules of which do not ionise. It was to explain such abnormal results with electrolytes that Arrhenius put forward his theory of electrolytic dissociation.

**\* The strengths of acids.**—The purest water which can be obtained is almost, but not quite, a non-conductor of electricity. After allowing for the effects of traces of conducting impurities, a slight conductivity, due to the ions of water itself, remains.

The ions of water are the hydrogen ion,  $\text{H}^+$  and the hydroxide ion,  $\text{OH}^-$ .

If 1 mol of hydrochloric acid is dissolved in water so that the total volume of solution is 1 litre, the conductivity of the water is increased nearly ten millionfold.

Most acids, bases and salts, such as hydrochloric acid, sulphuric acid, acetic acid, caustic potash, lime, common salt, copper sulphate, and alum, give conducting solutions with water, and are electrolytes (p. 201). Pure sugar, urea, alcohol, and most organic compounds, however, do not give conducting solutions with water: they are non-electrolytes. Since acids may be regarded as hydrogen salts, and bases as salts containing the hydroxide radical,  $\text{OH}$ , the results described may be summarised in the statement that nearly all salts are electrolytes.

Since acids in solution owe their acidic properties to the hydrogen ion, their *relative strengths* may be compared by



measuring the relative ionisations in solutions containing equivalent weights of the acids in identical volumes. The ionisation is most conveniently determined by the conductivity of the solution. Since the hydrogen ion is much more mobile than any of the anions of acids, it carries most of the current, and the relative conductivities of different acids are therefore approximately proportional to the ionisations.

One-fiftieth normal ( $N/50$ ) solutions of acetic, sulphuric, and hydrochloric acids, and pure water are poured into four glass tubes, fitted with platinum electrodes, as shown in Fig. 154.

The electrodes are set at the same distance apart in the four tubes, and in series with each tube is a carbon-filament lamp. The tubes are connected in parallel with the lighting mains. The lamps in circuit with the water and acetic acid remain dark, because the conductivity is so small that practically no current passes. The lamps connected with the hydrochloric and sulphuric acids light up, showing that the solutions are good conductors. Acetic acid is a *weak acid*: it is only slightly ionised in solution. Hydrochloric and sulphuric acids are *strong acids*, largely ionised in solution.

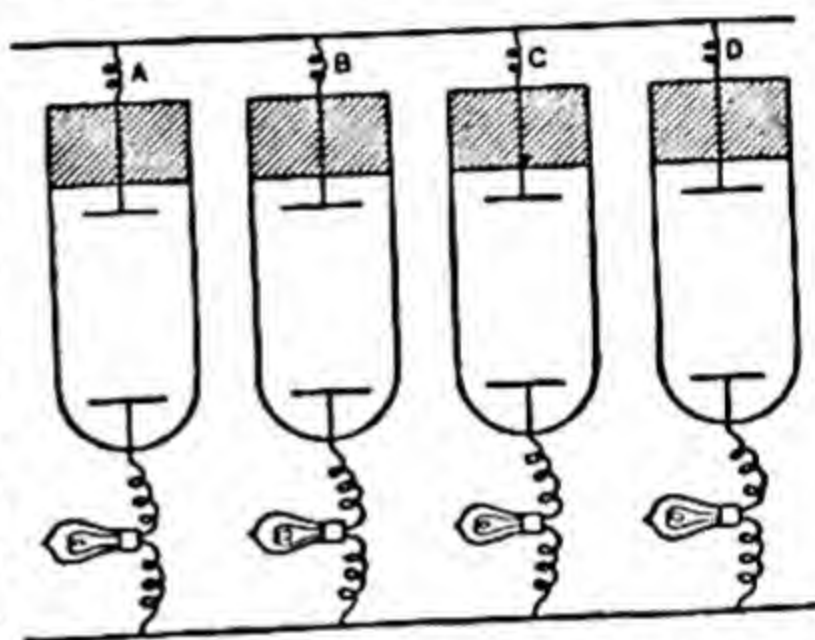
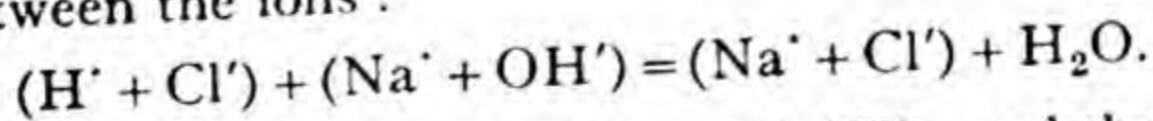


FIG. 154.—CONDUCTIVITIES OF ACIDS.

**Neutralisation.**—Acids are substances producing the hydrogen ion in solution:  $\text{HCl} = \text{H}^+ + \text{Cl}'$ . Bases are substances producing the hydroxide ion in solution:  $\text{NaOH} = \text{Na}^+ + \text{OH}'$ .

If an acid and a base in solution are mixed, a salt is formed, and the solution becomes neutral. This is usually represented by such equations as:  $\text{HCl} + \text{NaOH} = \text{NaCl} + \text{H}_2\text{O}$ . Since the acid, base, and salt are ionised in solution, the reaction really occurs between the ions:



It will be seen that the anion of the acid ( $\text{Cl}'$ ), and the cation of the base ( $\text{Na}^+$ ), which together constitute the ions of the salt, take no part in the change: they are free before and after the reaction. The net change in neutralisation is the union of the hydrogen ion of the acid with the hydroxide ion of the base to form practically undissociated water:  $\text{H}^+ + \text{OH}' = \text{H}_2\text{O}$ .

This is the sole reaction with strong acids and bases, *i.e.*, those which are practically completely ionised. Salts are nearly always largely ionised in solution.

The hydrogen ions and hydroxide ions are those which possess the greatest mobility (p. 207). After neutralisation, therefore, when the rapid hydrogen and hydroxide ions have been withdrawn, the conductivity of the solution will be appreciably diminished.

This is demonstrated by the following experiment. A solution of caustic soda is poured into a rectangular glass cell fitted with parallel electrodes (Fig. 155). A solution of hydrochloric acid

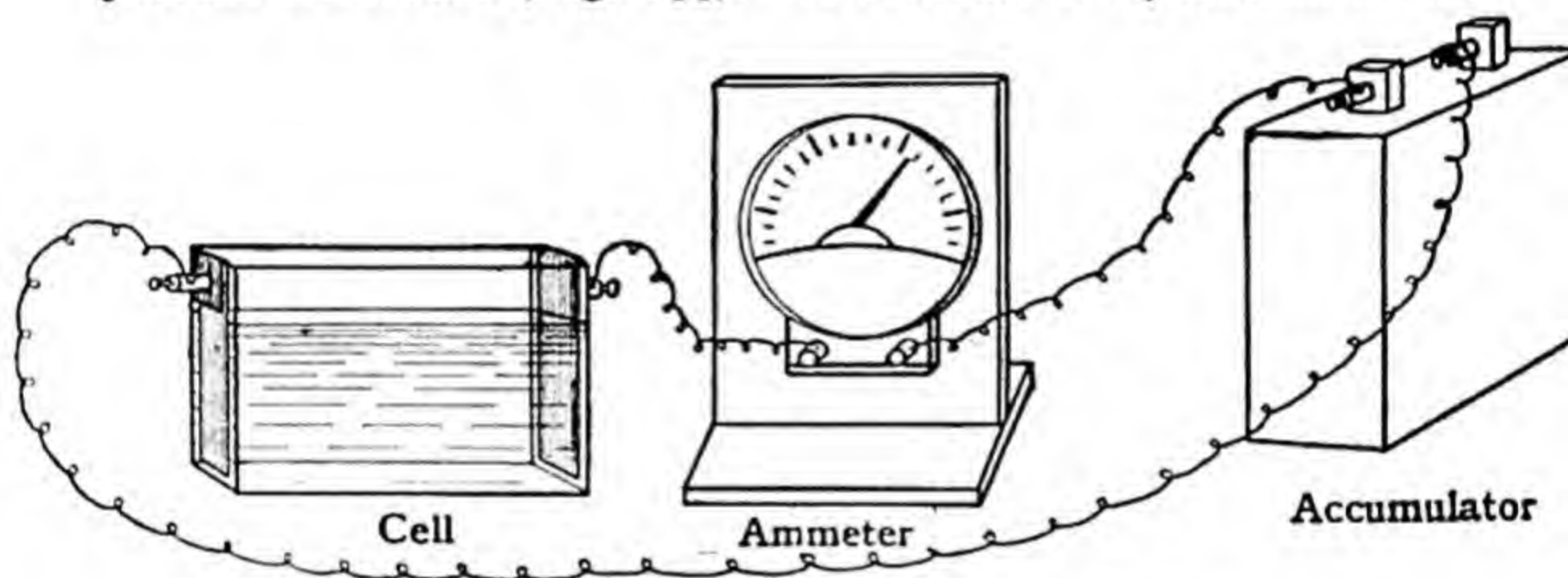


FIG. 155.—APPARATUS TO DEMONSTRATE DIMINUTION IN CONDUCTIVITY ON NEUTRALISATION.

is carefully stratified over the alkali solution by running it from a pipette on a piece of cork floating on the alkali. The current is switched on and the ammeter reading noted. The current is carried by the ions  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ ,  $\text{Cl}^-$ . Now the solutions are stirred. The ions  $\text{H}^+$  and  $\text{OH}^-$  disappear to form  $\text{H}_2\text{O}$  (un-ionised) and the current is reduced, as shown by the ammeter reading.

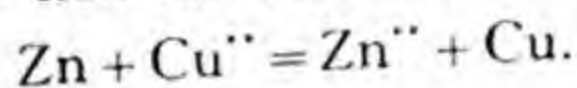
**\* Ions in solid salts.**—According to the modern theory, the charged *ions* of salts are present as such even in the crystals. In the sodium chloride crystal in Fig. 142 the sodium and chlorine particles are really sodium and chlorine *ions*: the whole crystal is an assemblage of positive and negative ions occupying the lattice points: there are no *molecules* of sodium chloride as such in the crystal. Even in solution it is now thought that the sodium chloride is practically *completely* ionised. The vapour density of sodium chloride, determined at very high temperatures, corresponds with the formula  $\text{NaCl}$ , so that sodium chloride molecules can exist in the form of vapour.



Substances such as water, ammonia, hydrogen chloride gas, alcohol, and many solids which do not form electrolytically conducting solutions exist, of course, in the form of uncharged molecules. In the case of electrolytes such as sodium chloride *the charged ions are not produced when the salt is dissolved but are already present in the solid crystals.* They are also set free to move when the salt is fused, so that fused salts also conduct the electric current, and, as Faraday showed, they obey the laws of electrolysis.

When hydrochloric acid gas is dissolved in water, an electron passes from the hydrogen atom to the chlorine atom, so that a positive hydrogen ion and a negative chloride ion are produced, which then exist free in the solution.

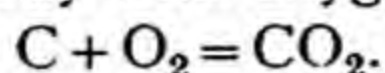
One metal (*e.g.*, zinc) displaces the ions of another (*e.g.*, copper) from solution when its atom tends to lose electrons more readily, *i.e.*, to form ions. These electrons are forced upon the dissolved metal ions and the neutral atoms of the second metal are deposited :



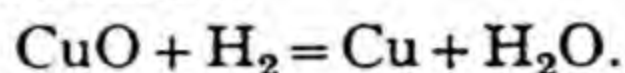
**\*Positive and negative valencies.**—Although sodium, potassium, chlorine and bromine are all univalent in the compounds NaCl, KBr, NaBr and KCl, yet their atoms cannot replace one another in any order if the general properties of the compounds are to be maintained. Potassium may replace sodium, and bromine may replace chlorine, but sodium cannot replace chlorine, or bromine potassium. For this reason, valencies are classified as **positive** and **negative**: sodium and potassium are called **electro-positive** elements, and chlorine and bromine are **electro-negative**. This nomenclature is derived from the facts of electrolysis: the modern views on atomic structure are also in agreement with it; we may say that the valency of sodium is +1, that of chlorine is -1. The same system may be extended to radicals; for example, the valency of the  $\text{SO}_4$  radical is -2, that of the ammonium radical +1, and so on. The valency of an ion (*q.v.*) is equal in sign and magnitude to its charge. This method of considering valency is especially useful in the study of oxidation and reduction.

From the point of view of atomic structure (p. 250), the *positive* valency of an element in its compounds is equal to the number of (negative) electrons *lost* by the atom; the *negative* valency is equal to the number of electrons *gained* by the atom. Thus, when potassium reacts with bromine, the potassium atom loses one electron, which is transferred to the bromine atom.

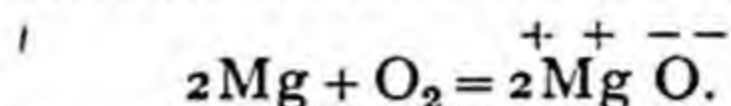
The simplest type of oxidation reaction is that in which a substance combines directly with oxygen:



The simplest type of reduction reaction is that in which oxygen is removed from a substance:

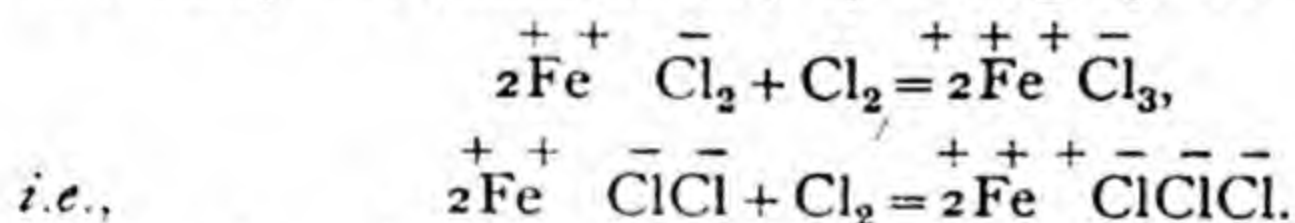


When a substance combines with oxygen it gives up electrons to the oxygen, and since it loses negative electrons *the positive valency of the substance oxidised is increased*:



The valency of magnesium in MgO is +2, that of oxygen -2. The valencies in the *free* states (metallic magnesium; oxygen gas) are taken as zero.

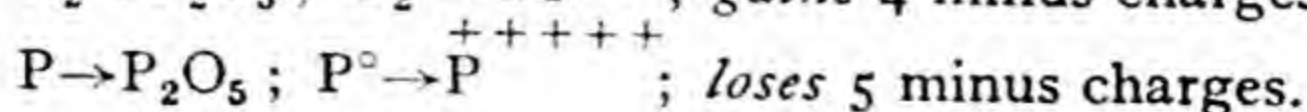
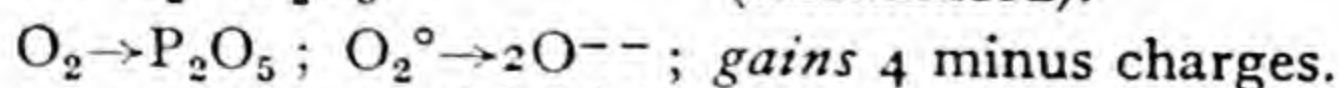
*Substances which contain atoms capable of taking up electrons are oxidising agents.* Oxygen readily takes up electrons, and is an oxidising agent. When ferrous chloride is converted into ferric chloride, the iron is oxidised, because its positive valency is increased from +2 to +3, and if the change is effected by means of free chlorine the latter is changed from zero valency to valency -1 (chloride ion) by taking up electrons:



Chlorine, therefore, in accordance with our definition, is an oxidising agent: in the change it becomes reduced to chloride ions by taking up electrons. Thus, *reduction is an increase in negative valency.* A *reducing agent* (e.g., the ferrous chloride) *must contain an atom capable of providing electrons.*

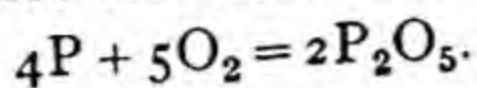
It is clear that, since there is no change of net charge in a reaction, the oxidising agent must take up the electrons furnished by the reducing agent, and that *oxidation and reduction must occur simultaneously.* This provides a method of balancing equations which is sometimes convenient, and is illustrated by the following examples in increasing order of difficulty.

(1) *Oxidation of phosphorus.*



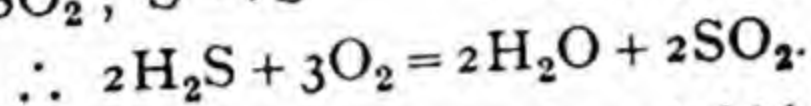
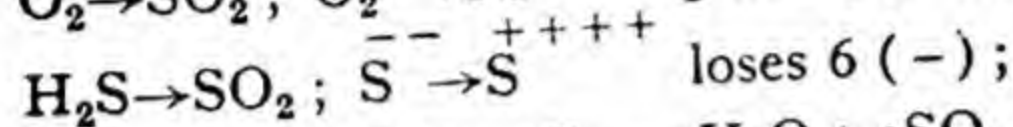
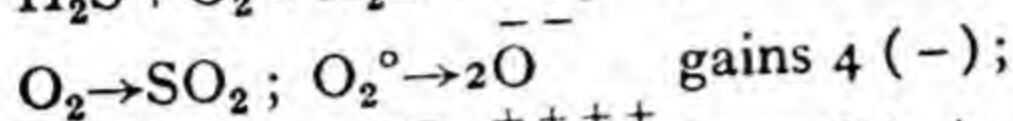
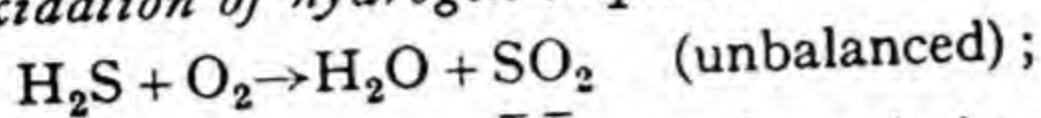


The least common multiple of 4 and 5 is 20;  $\therefore$  there must be a *gain* of 20 electrons by the oxygen and a *loss* of 20 electrons by the phosphorus, hence the balanced equation is :

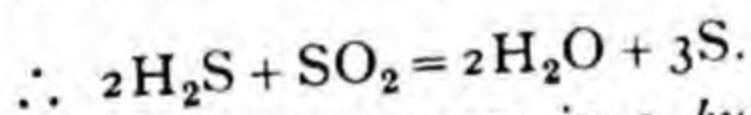
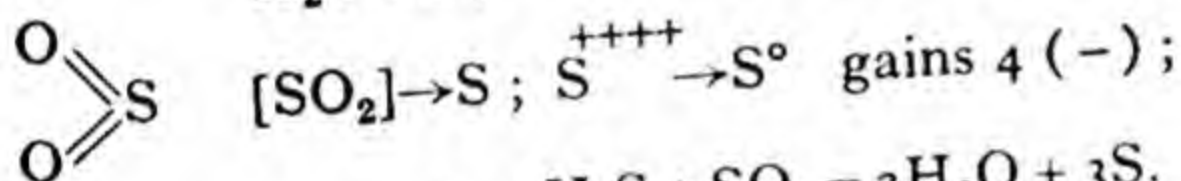
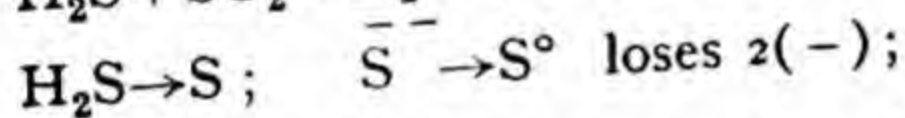
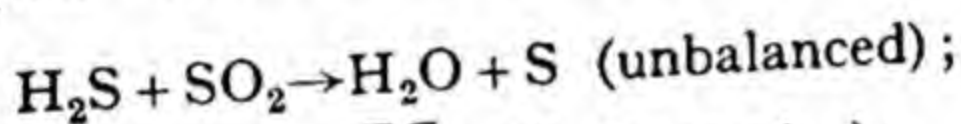


(Note.—All *free* elements are taken of zero valency.)

(2) *Oxidation of hydrogen sulphide.*

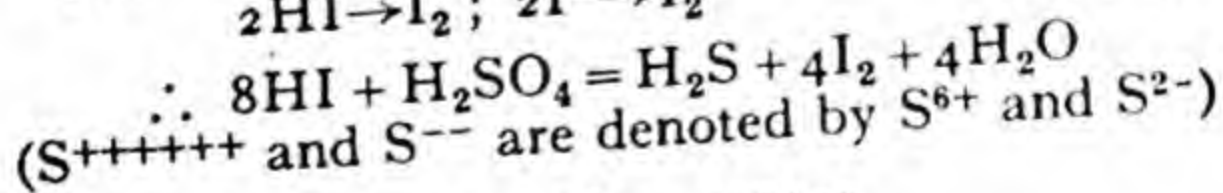
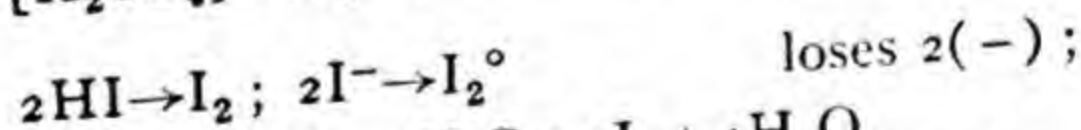
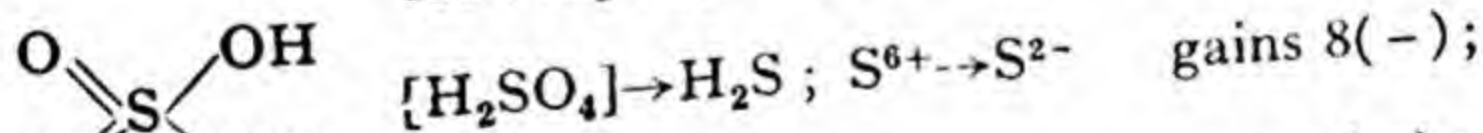
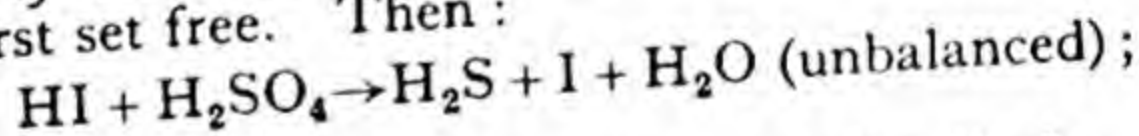


(3) *Reaction between hydrogen sulphide and sulphur dioxide.*



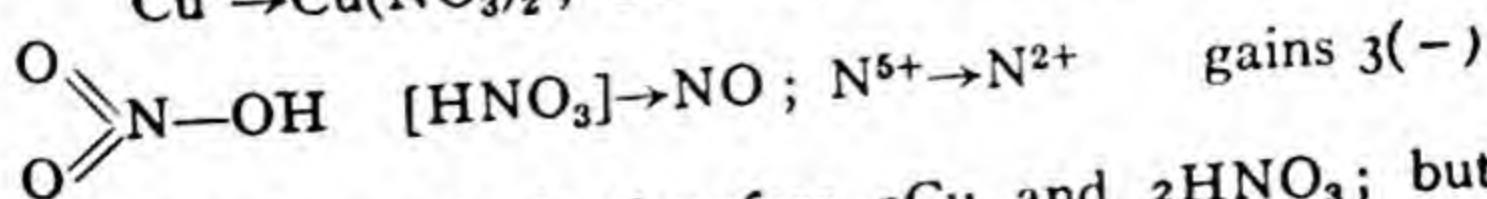
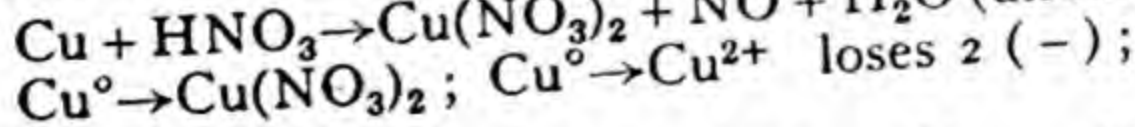
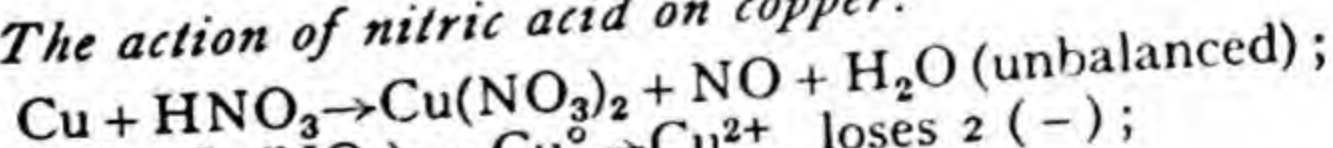
(Note.—The valency of an element in a *hydrogen* compound is *negative*; in an *oxide* it is *positive*.)

(4) *The action of hot concentrated sulphuric acid on potassium iodide.* HI is first set free. Then :



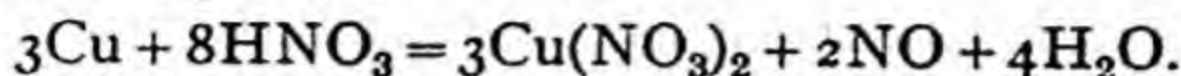
( $\text{S}^{++++}$  and  $\text{S}^{--}$  are denoted by  $\text{S}^{6+}$  and  $\text{S}^{2-}$ )

(5) *The action of nitric acid on copper.*

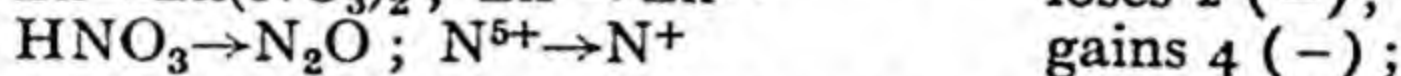
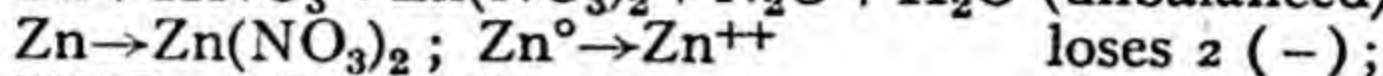
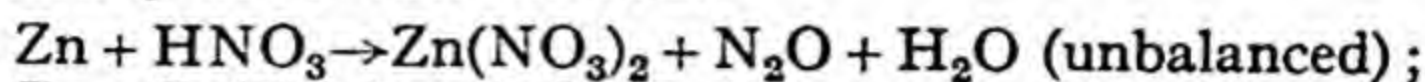


The oxidation ratio is therefore 3Cu and 2HNO<sub>3</sub>; but the

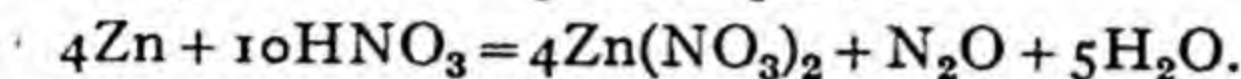
$3\text{Cu}^{++}$  ions require  $6\text{NO}_3^-$  ions, hence  $8 = 2 + 6$  molecules of nitric acid are required :



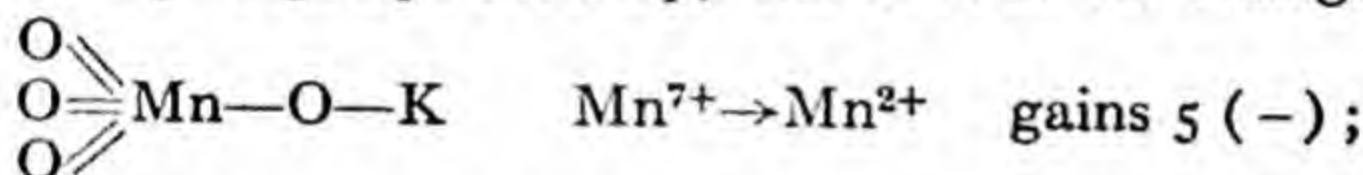
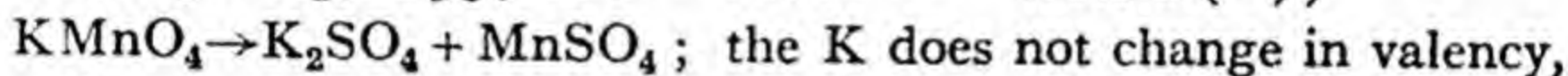
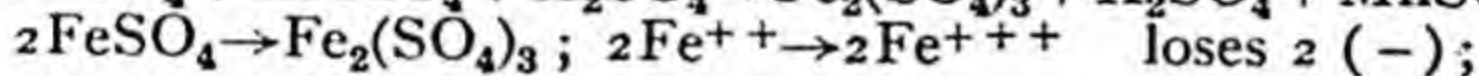
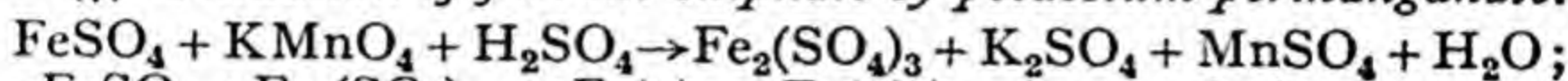
(6) *Action of nitric acid on zinc.*



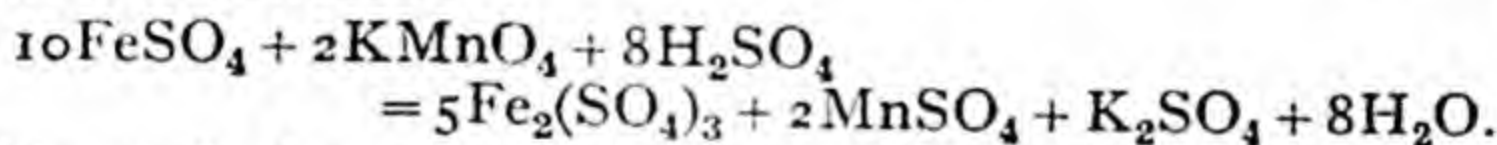
$\therefore 4\text{Zn}$  and  $2\text{HNO}_3$  are required, but the  $4\text{Zn}^{++}$  ions require  $8\text{NO}_3^-$  ions;  $\therefore 10\text{HNO}_3$  are required :



(7) *Oxidation of ferrous sulphate by potassium permanganate.*



$\therefore 10\text{FeSO}_4$  and  $2\text{KMnO}_4$  are required; the  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ , and  $\text{K}^+$  ions will require altogether  $15 + 1 + 2 = 18\text{SO}_4$  ions, of which 10 are provided by the  $10\text{FeSO}_4$ , hence  $18 - 10 = 8\text{H}_2\text{SO}_4$  are required in addition :



This method should be practised in connection with various equations to be met with in the rest of the book.

**\*Voltaic cells.**—An arrangement in which chemical energy is converted into electrical energy is called a voltaic cell, since the first representative of this type of apparatus was invented by Volta in 1800. The simple cell devised by Volta consists of a plate of zinc and one of copper immersed in dilute sulphuric acid. When the plates outside the liquid are joined by a wire, the zinc dissolves, but the hydrogen bubbles are evolved from the copper, not from the zinc (Fig. 156). An electric current, recognised by its heating and magnetic effects, flows through the wire. The direction of flow of positive electricity is taken conventionally as the direction of the current, although it is really negative electricity, in the form of electrons, which flows through conductors in the opposite direction (p. 205). With the usual convention the direction of the current is from the



copper to the zinc outside the cell. Since the current must be completed inside the cell, the positive electricity passes in the latter from the zinc to the copper. This is effected by the transport of positive charges by the hydrogen ions moving in this direction. The hydrogen ions are deposited on the copper plate, give up their charges to it, and appear as gaseous hydrogen. The discharge may be regarded as due to the removal of free electrons from the copper plate, which neutralise the positive hydrogen ions:  $H^+ + e = H$ .

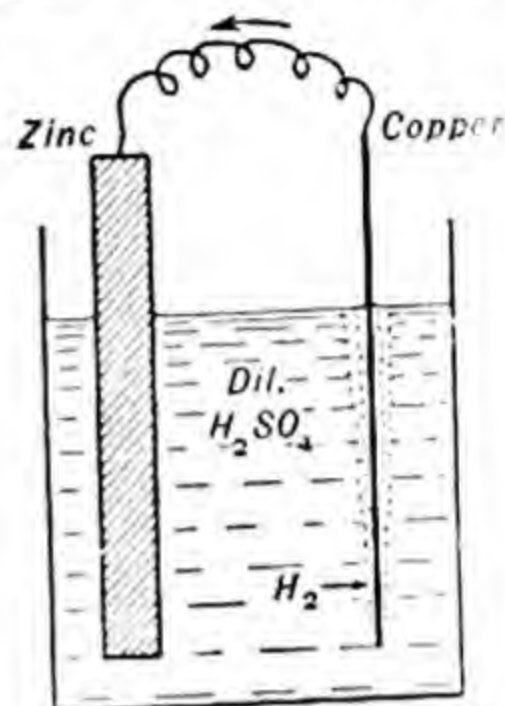


FIG. 156.—THE SIMPLE CELL.

The negative charge taken from the copper is replaced by a current of negative electrons flowing along the wire from the zinc to the copper, *i.e.*, in the opposite direction to the conventional positive current. These electrons must come from the zinc. The latter dissolves as positively charged zinc ions, and the positive charges of the latter are derived by the abstraction of electrons from the zinc atoms:  $Zn - 2e = Zn^{++}$ . These electrons remaining in the zinc pass along the wire to, and neutralise the hydrogen ions arriving at, the copper plate.

If the zinc had merely dissolved in the acid without producing current, the hydrogen ions of the acid would have been neutralised in contact with the metal when the latter passed into solution in the ionic state, and hydrogen gas would have been evolved from the surface of the zinc. In the cell, the neutralisation of the hydrogen ions, with production of hydrogen gas, still takes place on account of the negative charge left by the ionisation of the zinc, but the hydrogen ions travel through the liquid to the copper plate in order to pick up this charge, so that the two reactions, which when they occur in the same place give out only heat, when they are compelled to take place at *two different localities* produce a current. This is sometimes called 'chemical action at a distance.'

Ordinary zinc contains traces of other metals, such as iron, and the specks of these metals lying on the surface of the zinc act like copper plates in the cells. Hydrogen gas is really given off from the second metal, and the current (which passes round the wire connecting the plates) flows through the zinc from the points where solution occurs to the parts where the impurities lie on the

surface. Action of this kind is called **local action**. If the surface of the zinc is amalgamated, or if very pure zinc is used, the impurities are removed, and the surface is uniform. The metal then no longer evolves hydrogen in dilute acid, since local action is no longer possible. If, however, the zinc is touched under the surface of the acid with a piece of copper or platinum wire, bubbles of hydrogen are at once evolved from the wire, and the zinc dissolves.

The voltaic cell does not generate *electricity*. The electrical charges are present in the chemical substances used in making up the cell, in the form of electrons, and the electrons are added to, or subtracted from, atoms to form ions. Some of these ions (*e.g.*, hydrogen ions) are discharged in the cell, and other previously uncharged substances (*e.g.*, zinc) are converted into ions. The electrons leaving one atom and attaching themselves to another are driven round the outside conducting wire. All the electrons remain in the materials of the cell, but in new combinations, and none is set free. During this transfer of electricity, *energy* may be taken from the battery.

The voltage of the Volta cell is about 0.74; a large number of these cells connected in series, *i.e.*, with the zinc of one connected with the copper of the next, formed the battery used by Davy in 1807 for the decomposition of the alkalis: they are still shown at the Royal Institution in London.

**\*The Daniell cell.**—The Volta cell has the disadvantage that its electromotive force, or voltage, rapidly decreases when

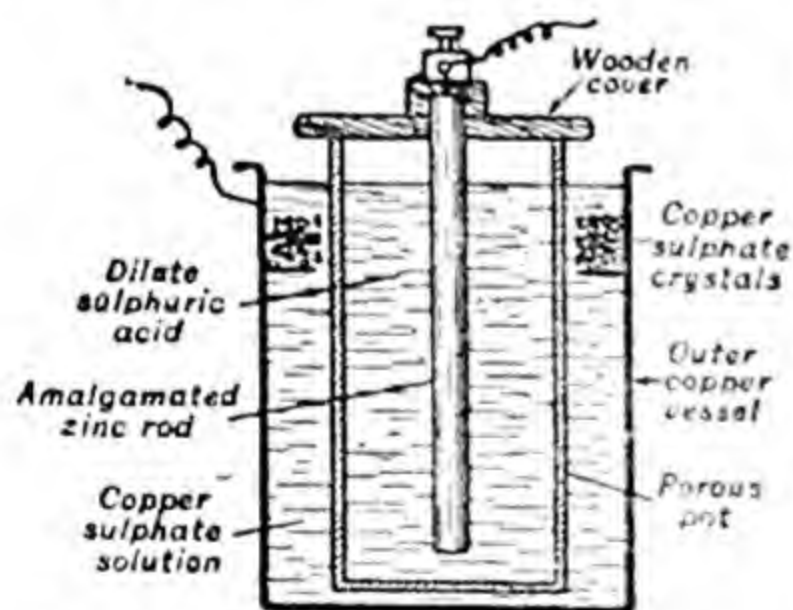


FIG. 157.—THE DANIELL CELL.

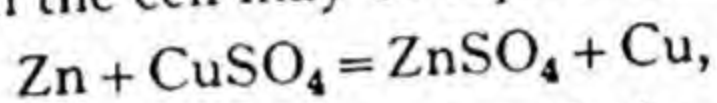
current is taken from it. In another type of cell, invented by Daniell (1836), the voltage remains practically constant during action. This cell consists (Fig. 157) of a rod of amalgamated zinc immersed in dilute sulphuric acid, and a copper container holding a solution of copper sulphate. The two solutions are separated by a pot of unglazed earthenware, which prevents them from mixing but

permits the passage of ions moving from one liquid to the other. The voltage of this cell is about 1.09.

The action of the Daniell cell is as follows. The zinc dissolves in the dilute acid as zinc ions, and the copper ions deposit



from the copper sulphate solution as metal. No gas is evolved, since the hydrogen ions passing from the liquid round the zinc, through the porous partition, are not deposited but remain in the copper sulphate solution. Instead of hydrogen ions being deposited on the copper, copper ions, which are more easily discharged, give up their charges to, and form a coating of copper on, the copper container. For every equivalent of copper deposited, an equivalent of hydrogen ions enters the copper sulphate solution, forming sulphuric acid, leaving an equivalent of  $\text{SO}_4^{--}$  ions in the zinc compartment, which form zinc sulphate with the zinc ions given off by the zinc plate. The dilute sulphuric acid is gradually converted into a solution of zinc sulphate whilst the copper sulphate solution is turned into dilute sulphuric acid, so that the reaction in the cell may be represented by the equation :

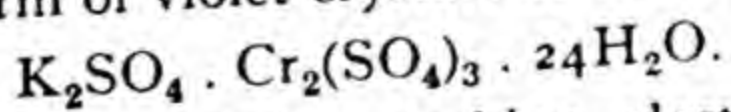


or, since the two salts are ionised and the  $\text{SO}_4^{--}$  ion remains unchanged, as :  $\text{Zn} + \text{Cu}^{++} = \text{Zn}^{++} + \text{Cu}.$

Thus, two negative electrons are removed from the zinc atom, forming a zinc ion, which passes into solution, and two electrons travel round the wire to the copper pole, where they attach themselves to a copper ion in solution, forming a neutral atom of copper, which is deposited.

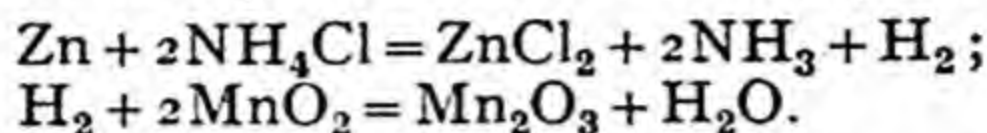
We may regard the action as due to the greater tendency of zinc atoms to throw off electrons, forming ions, than of copper atoms to undergo a similar change. Metals may be arranged in an **electromotive series**, the higher members of which have a greater tendency to lose electrons than the lower members, and can, therefore, displace the latter from solutions of their ions, in the form of metals.

In the **dichromate cell**, zinc and carbon are immersed in a solution of sodium or potassium dichromate acidified with dilute sulphuric acid. The chromic acid,  $\text{CrO}_3$ , set free, is reduced by the hydrogen deposited on the carbon plate in presence of sulphuric acid to chromic sulphate,  $\text{Cr}_2(\text{SO}_4)_3$ , and if potassium dichromate has been used the potassium sulphate simultaneously formed may crystallise out with the chromic sulphate in the form of violet crystals of chrome alum :



The **Leclanché cell**, used for working electric bells, consists of a zinc rod in a solution of sal-ammoniac (ammonium chloride) : the positive pole consists of a carbon plate inside a porous pot

packed with crushed carbon and manganese dioxide to act as a depolariser, *i.e.*, to remove by oxidation the hydrogen which would otherwise be deposited on the carbon plate :



In dry cells, the zinc forms an outer cylinder, inside which is the ammonium chloride and manganese dioxide, mixed with glycerin and gelatin, and a carbon rod in the centre.

The cells described above are called **primary cells**, since an electric current is set up directly by the chemical changes occurring in them. Another type of cell is the **secondary cell**, which is first 'charged' by passing an electric current through it, and then in turn itself yields a current. The most important example of such a cell is the **lead accumulator**.

**\*The lead accumulator.**—The accumulator (Fig. 158) consists of two lead gratings, one filled with finely divided lead and the other with a higher oxide of lead, lead dioxide,  $\text{PbO}_2$ , both

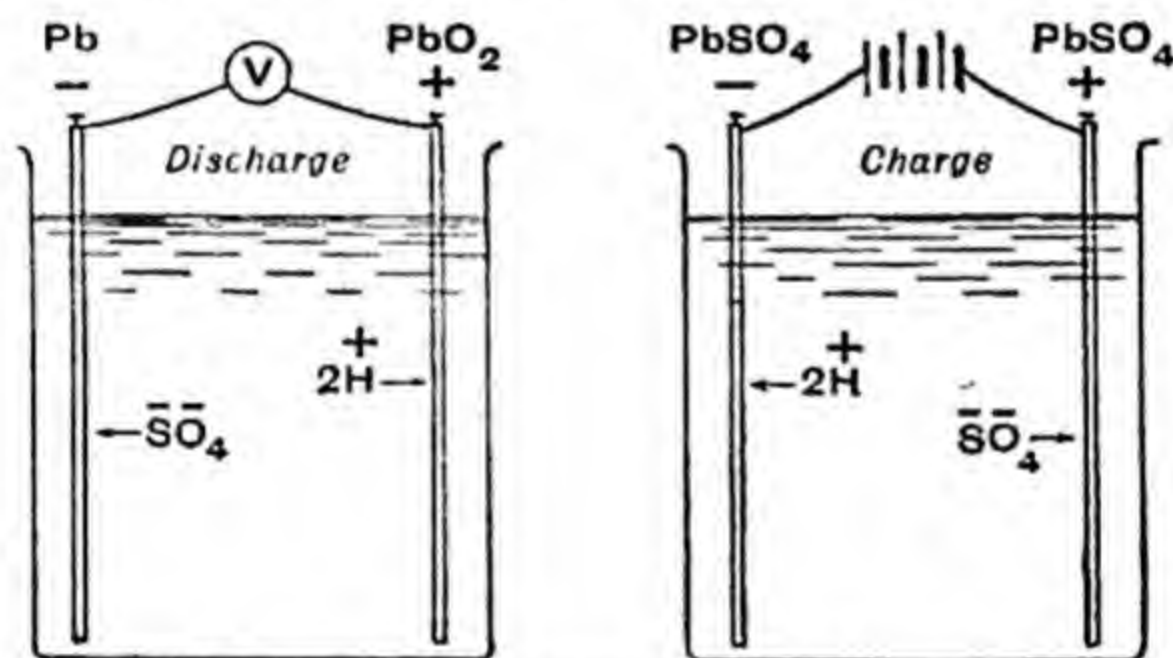
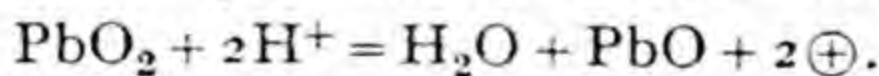
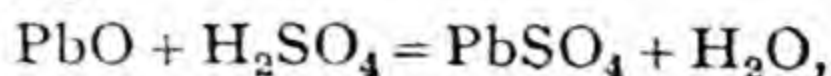


FIG. 158.—CHEMICAL REACTIONS IN THE LEAD ACCUMULATOR.

immersed in dilute sulphuric acid. The acid is ionised into hydrogen ions ( $2\text{H}^+$ ) and sulphate ions ( $\text{SO}_4^-$ ). When the battery is *furnishing current*, the  $\text{H}^+$  ions move to the peroxide plate, are deposited on it and give up their positive charge to it, making it the anode or positive pole of the cell. The hydrogen then reduces the lead peroxide to a lower oxide of lead, **lead monoxide** :



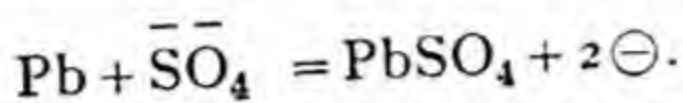
The monoxide is at once converted by the sulphuric acid into lead sulphate,  $\text{PbSO}_4$  :





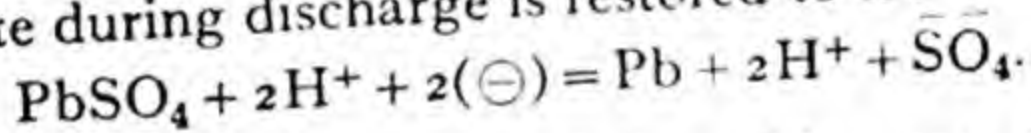
a reaction not involving the transfer of charges, but occurring spontaneously.

Whilst the  $H^+$  ions of the sulphuric acid are migrating to the peroxide plate, the  $\bar{S}\bar{O}_4$  ions are finding their way to the lead plate; they deposit on it, give it a negative charge, so making it the cathode, and convert it into lead sulphate:

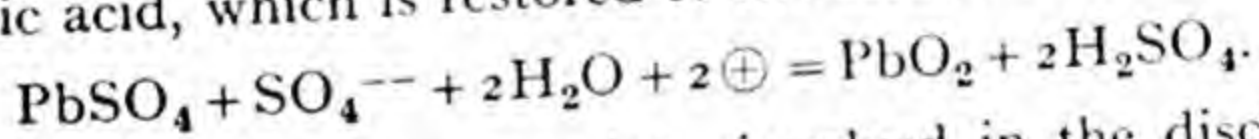


Both plates, therefore, tend to become converted into lead sulphate, and sulphuric acid is withdrawn from the solution, hence the state of charge is easily found by measuring the density of the solution by a hydrometer.

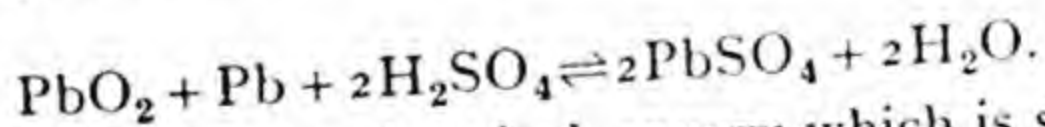
To *recharge* the accumulator, current from a dynamo is passed through it in the opposite direction to the current furnished by the cell, *i.e.*, the positive (red) pole of the cell is connected with the positive of the dynamo and the negative of the cell to the negative of the dynamo. The  $H^+$  ions of the acid now pass to the cathode, and an  $SO_4^{--}$  ion is produced from the insoluble lead sulphate, so that the plate is again reduced to lead and the sulphuric acid which was taken from the solution by this plate during discharge is restored to it:



At the same time the  $\bar{S}\bar{O}_4$  ion of the acid passes to the anode, deposits on it, forming lead peroxide and, in presence of water, sulphuric acid, which is restored to the solution:



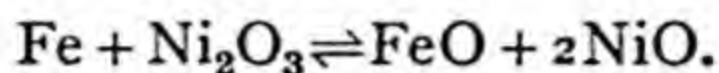
It will be seen that the reactions involved in the discharging and charging of a lead accumulator can be represented by the equation:



It is not electricity or electrical energy which is stored in the cell, but *chemical energy*; the material  $PbSO_4$  is converted by the expenditure of electrical energy in the cell (leading to the chemical reactions of charging) into the two materials of a primary cell. In the Daniell cell the energy was spent outside the cell in the reduction of the zinc ore to metallic zinc in the smelting process. But whereas the reaction in the Daniell cell is not conveniently reversed by an electric current, so as to put the cell into its initial active form, that in the accumulator is

easily reversed by an electrolytic method, with an expenditure of energy practically the same as that obtained in the action of the cell. The latter, therefore, acts as a *reservoir of energy*.

The **Edison accumulator** consists of finely divided iron and a higher oxide of nickel in a solution of caustic potash. The iron is first converted into ferrous oxide and at the same time the nickel peroxide is reduced to nickel monoxide. In charging the cells the reactions are reversed :

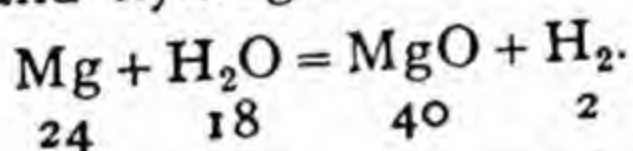




## CHAPTER XIV

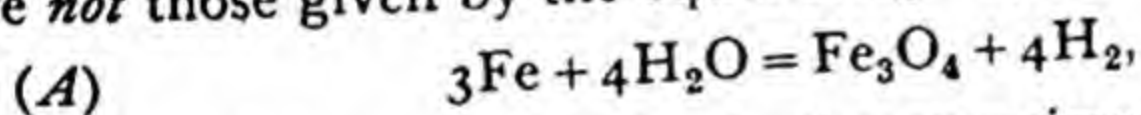
### CHEMICAL EQUILIBRIUM

**Reversible reactions and equilibrium.**—Reactions as represented by equations may sometimes proceed so that the chemical change is complete. When a given weight of water in the form of steam is passed over red-hot magnesium the weights of magnesium oxide and hydrogen formed are as given by the equation :

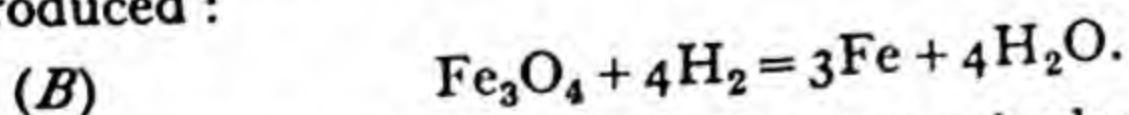


Hydrogen passed over red-hot magnesium oxide does not reduce it to magnesium : the reaction is not reversible.

But if a given weight of water is passed in the form of steam over red-hot iron, the weights of black iron oxide and hydrogen are *not* those given by the equation (p. 292) :



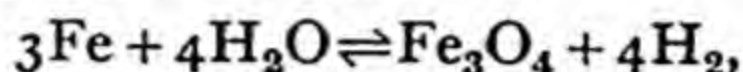
because, no matter how slowly the experiment is performed, a considerable amount of the steam passes on undecomposed and a corresponding amount of iron is left unchanged if the weight of water used is that corresponding with the equation. The explanation of this result becomes clear from a further experiment. When hydrogen is passed over red-hot black oxide of iron, the oxide is reduced and water in the form of steam is produced :



Here again it will be found that some hydrogen always passes on with the steam, so that unless a large excess of hydrogen is used the reaction is incomplete.

These results are easily explained if we assume that *both reactions A and B take place at the same time*, so that when steam is passed over iron, the hydrogen formed tends to reduce the oxide of iron again, and when hydrogen is passed over iron

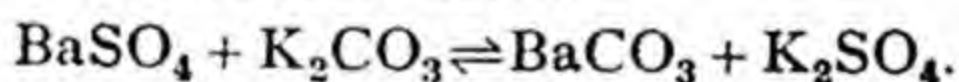
oxide the steam formed tends to oxidise the iron again. In actual fact, if a mixture of hydrogen and steam in the correct proportions is passed over a heated mixture of iron and oxide of iron, no change at all occurs either in the gas or in the solid mixture: the one mixture is therefore in chemical equilibrium with the other. The fact that such a state is possible depends on the reversibility of the reaction:



as denoted by the double arrows. *Equilibrium is attained when two opposing reactions proceed with equal speeds.* The same equilibrium state is reached by starting either with iron and steam or with iron oxide and hydrogen.

If a given weight of iron is taken, and a *considerable excess* of steam passed over it, the red-hot iron will ultimately be completely oxidised, and similarly a given weight of iron oxide will, when heated to redness and exposed to a current of hydrogen in considerably greater amount than is required by the chemical equation, ultimately be completely reduced.

Dulong found that if barium sulphate is boiled with successive quantities of potassium carbonate solution it is gradually completely converted into barium carbonate; whilst barium carbonate, when boiled with successive quantities of potassium sulphate solution, is entirely transformed into barium sulphate; the reaction is therefore reversible:



Both  $\text{BaSO}_4$  and  $\text{BaCO}_3$  are commonly supposed to be 'insoluble'; they are, however, very slightly soluble, and the reactions go on in solution.

The examples just cited illustrate what is sometimes called the action of mass.

The conception of the equilibrium state as *the balance of two opposing reactions* follows from the kinetic theory. A liquid comes into equilibrium with its vapour when as many molecules leap out of the liquid as return to it in a given interval. A salt is in equilibrium with its saturated solution when as many molecules break away from the solid per second as are caught up again, possibly in a different part of the crystal. If barium peroxide is heated in a closed vessel at a constant temperature, it decomposes into baryta and oxygen:  $2\text{BaO}_2 = 2\text{BaO} + \text{O}_2$ . The oxygen molecules, by collision with the baryta, reproduce molecules of barium peroxide. The higher the pressure of the

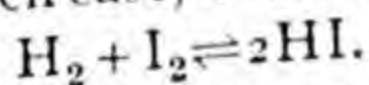


oxygen, the more frequent are the collisions of oxygen molecules on the baryta, and the greater is the rate of recombination.

The rate at which the peroxide molecules are breaking up is constant at a given temperature, hence, at a certain pressure of oxygen, the rate at which peroxide is reproduced becomes equal to the rate at which it is decomposed. A state of equilibrium is therefore set up at a definite pressure of oxygen, called the *dissociation pressure*:  $2\text{BaO}_2 \rightleftharpoons 2\text{BaO} + \text{O}_2$ . If the pressure of the oxygen is raised, the collisions become more frequent, additional combination takes place, and if the pressure is *maintained* above the dissociation pressure, *all* the oxygen is reabsorbed by the baryta. If the pressure of the oxygen is decreased, more peroxide decomposes, since less oxygen returns to it by collisions, and if gas is *continuously* pumped off, *all* the peroxide is ultimately decomposed. (The **Brin process** for the production of oxygen.)

The experimental fact that the pressure of oxygen in equilibrium depends only on the temperature and not on the relative surfaces of barium monoxide and peroxide exposed to the collisions of oxygen molecules shows that the reaction takes place at the *surface of separation* between the two solids, as was pointed out many years ago by Ostwald.

**The effect of concentration: the law of 'mass action.'**—When a mixture of hydrogen and iodine vapour is heated, gaseous hydrogen iodide is formed, but the reaction is incomplete; and when hydrogen iodide is heated it is incompletely decomposed into hydrogen and iodine vapour. In each case, a state of equilibrium is reached:



The rate of formation of HI is proportional to the number of collisions per second of hydrogen and iodine molecules. These are proportional to the numbers of hydrogen and iodine molecules in unit volume, and the rate of formation of HI is proportional to the product of these. To avoid the use of very large numbers, the number of *gram molecules* (or *mols*) per litre is used; this is called the *concentration* and denoted by  $c$  (or sometimes the symbol in square brackets  $[\text{H}_2] = c_{\text{H}_2}$ , etc.). The rate of formation of HI in g. mols. per unit time per unit volume is thus  $k_1 c_{\text{H}_2} c_{\text{I}_2}$ , where  $k_1$  is called the *velocity coefficient*.

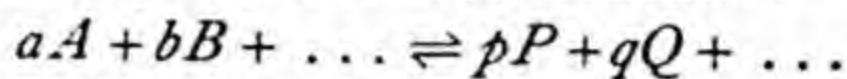
The rate of decomposition of HI is given by  $k_2 c_{\text{HI}}^2$ , since *two* molecules must collide. In equilibrium, hydrogen iodide is formed at just the same rate as it decomposes, hence, at a given temperature:

$$k_1 c_{\text{H}_2} c_{\text{I}_2} = k_2 c_{\text{HI}}^2 \quad \text{or} \quad c_{\text{HI}}^2 / c_{\text{H}_2} c_{\text{I}_2} = k_1 / k_2 = \text{const.} = K,$$

where  $K$  is called the *equilibrium constant*.

This is an example of the law of mass action, first perceived by Wenzel (1777) and Berthollet (1799), but clearly stated by Guldberg and Waage in 1867: *the rate of reaction is proportional to the concentration of each reacting substance*. It holds for gases and for dissolved substances.

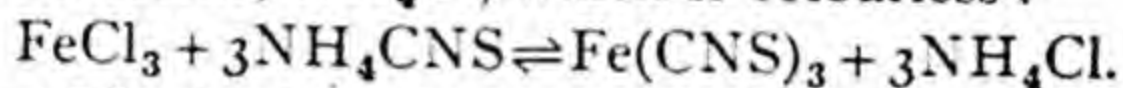
For the general type of reversible reaction :



the law of mass action takes the form :

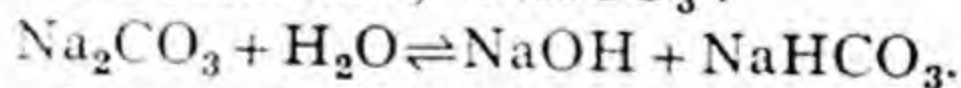
$$c_P^p c_Q^q \dots / c_A^a c_B^b \dots = K.$$

The law of mass action is illustrated by an experiment due to J. H. Gladstone (1855). Ferric chloride,  $\text{FeCl}_3$ , and ammonium thiocyanate,  $\text{NH}_4\text{CNS}$ , react in solution to produce ferric thiocyanate,  $\text{Fe}(\text{CNS})_3$ , which has a blood-red colour, and ammonium chloride,  $\text{NH}_4\text{Cl}$ , which is colourless :

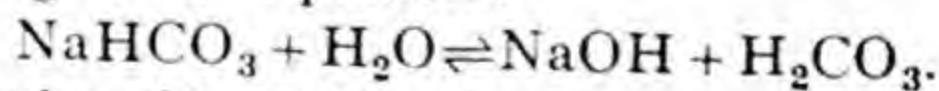


If excess of ferric chloride or ammonium thiocyanate is added, the blood-red colour deepens, since the reaction proceeds further from left to right, but if ammonium chloride solution is added the colour becomes much paler, since then the reaction proceeds further from right to left.

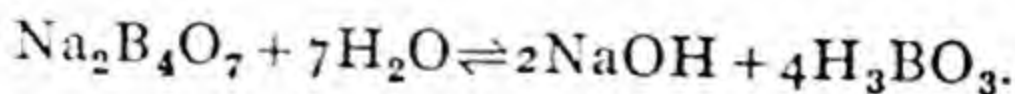
**Hydrolysis.**—A solution of caustic soda has a 'soapy' feel when rubbed between the fingers, and the same sensation is perceived to a less degree when a solution of washing soda or borax is used. Solutions of washing soda (sodium carbonate) and borax (sodium borate,  $\text{Na}_2\text{B}_4\text{O}_7$ ) also give a blue colour to red litmus or a red colour to phenolphthalein, reactions characteristic of **alkalies**. The two salts are, in fact, slightly decomposed by water, with the formation of some caustic soda. In the case of sodium carbonate, the other product of the reaction is mainly sodium bicarbonate,  $\text{NaHCO}_3$  :



Sodium bicarbonate itself shows alkaline properties, though not so powerfully as sodium carbonate. It is *slightly* decomposed according to the equation :



Since carbonic acid,  $\text{H}_2\text{CO}_3$ , is a very weak acid, the alkaline properties of the caustic soda are perceptible in the solution. Borax is decomposed into boric acid, a very weak acid, and caustic soda :

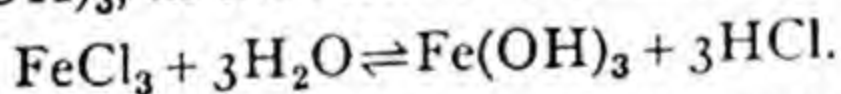




If phenolphthalein is added to a concentrated solution of borax, and then acetic acid till the pink colour just disappears, then on diluting the solution with water the pink colour appears again, showing that the reaction is reversible. (Boric acid has no action on phenolphthalein since it is a very weak acid.)

The liberation of *small* amounts of caustic 'alkali' by the action of water on washing soda, borax, and also soaps, is of importance in washing. Although the actual amount increases on dilution, yet the addition of more water keeps the concentration of alkali from rising to a point where it could become harmful to fabrics or the skin. The alkalinity of washing soda is, however, too great to allow it to be used in washing sensitive skins, and coarse soaps, containing too much free alkali, also roughen the skin and cause pain.

In other cases, salts when dissolved in water may yield *acid* solutions. This occurs when the acid is strong but the base weak, whereas in the cases studied above the base was strong and the acid weak. In many cases the base is insoluble and a clear solution of the salt cannot be obtained unless some acid is added, since otherwise the insoluble free base, or a basic salt, is precipitated. If a little concentrated ferric chloride solution,  $\text{FeCl}_3$ , is poured into a beaker of boiling distilled water a deep red solution is formed, which contains ferric hydroxide (the free base),  $\text{Fe}(\text{OH})_3$ , in the form of a colloidal solution (p. 176):



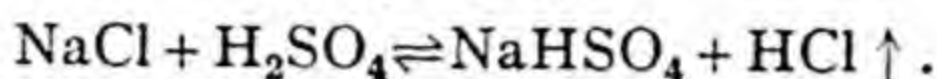
In a solution of ferric chloride, the ferric hydroxide,  $\text{Fe}(\text{OH})_3$ , which exists in the state of a colloidal solution (*cf.* p. 177), is a very weak base, practically not ionised, whilst the hydrochloric acid is largely ionised. Hence the solution has an acid reaction, from the presence of hydrogen ions:  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}'$ . The dark colour of the solution is due to the colloidal un-ionised base,  $\text{Fe}(\text{OH})_3$ .

The decomposition of a salt by water with production of free acid and base is called **hydrolysis**, and the reactions studied in this paragraph are examples of hydrolysis. The salt is said to be *hydrolysed* in solution, and the extent of hydrolysis usually increases with dilution, in accordance with the law of mass action.

**Effect of volatility or insolubility of a product of reaction.**—In many cases a reaction appears to go to completion, instead of reaching a state of equilibrium. Berthollet remarked that this often results from some *disturbance of the equilibrium state*, by

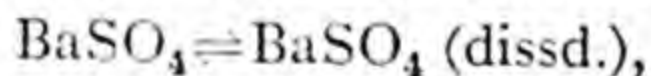
one or more of the products of the reaction being removed from the sphere of action by their *volatility*, or *insolubility*. As soon as they leave the system, passing into the gaseous state, or depositing as solids, they cease to exert any influence, and the reaction by which they are produced, being no longer opposed, cannot become balanced, and proceeds until the change becomes nearly, if not quite, complete.

Thus, if sulphuric acid is poured over common salt, a state of equilibrium is momentarily set up :

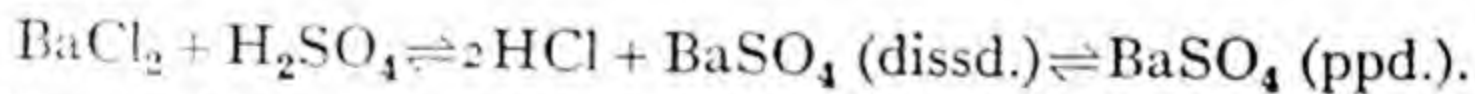


The hydrochloric acid, however, escapes from the liquid as a gas (shown by the upward-pointing arrow), the state of equilibrium is disturbed, and the reaction proceeds again. When the decomposition has reached the stage where the hydrochloric acid remaining is only sufficient to saturate the liquid, evolution of gas ceases, but if the gas is partly expelled by heating, further reaction occurs. Decomposition is, however, never quite complete.

If sulphuric acid is added to barium chloride solution, double decomposition ensues and a state of equilibrium is momentarily set up :  $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons 2\text{HCl} + \text{BaSO}_4 \downarrow$ . The barium sulphate, being very sparingly soluble, is precipitated (shown by the downward-pointing arrow) ; in this way it is removed from the sphere of action, and the reaction proceeds again. The sulphate, however, is really very slightly soluble, so that when the amount dissolved is in equilibrium with the solid,



a state of equilibrium is set up. The four substances are then in solution :



**Dissociation.**—The definition of dissociation given on p. 164 shows that the reaction is reversible, and hence a state of equilibrium may be set up. Since the products of dissociation recombine on cooling, it is necessary to adopt special methods to demonstrate the existence of dissociation, *e.g.*, vapour density determinations or diffusion. Another method depends on the *rapid cooling* of the dissociated product, when the rate of recombination becomes so small that the equilibrium at the higher temperature has no time to readjust itself to the altered conditions.



Grove (1847) heated a platinum wire in steam by an electric current. In contact with the hot wire, dissociation occurred and the products at once passed into the diluting atmosphere of steam, which prevented their recombination by separating them and by cooling them quickly.

Deville (1864) demonstrated the dissociation of steam at high temperatures by means of the apparatus shown in Fig. 159. A wide tube of glazed porcelain, with a narrower tube of unglazed porcelain supported axially inside, was heated strongly in a furnace. Water vapour was passed through the inner tube, and

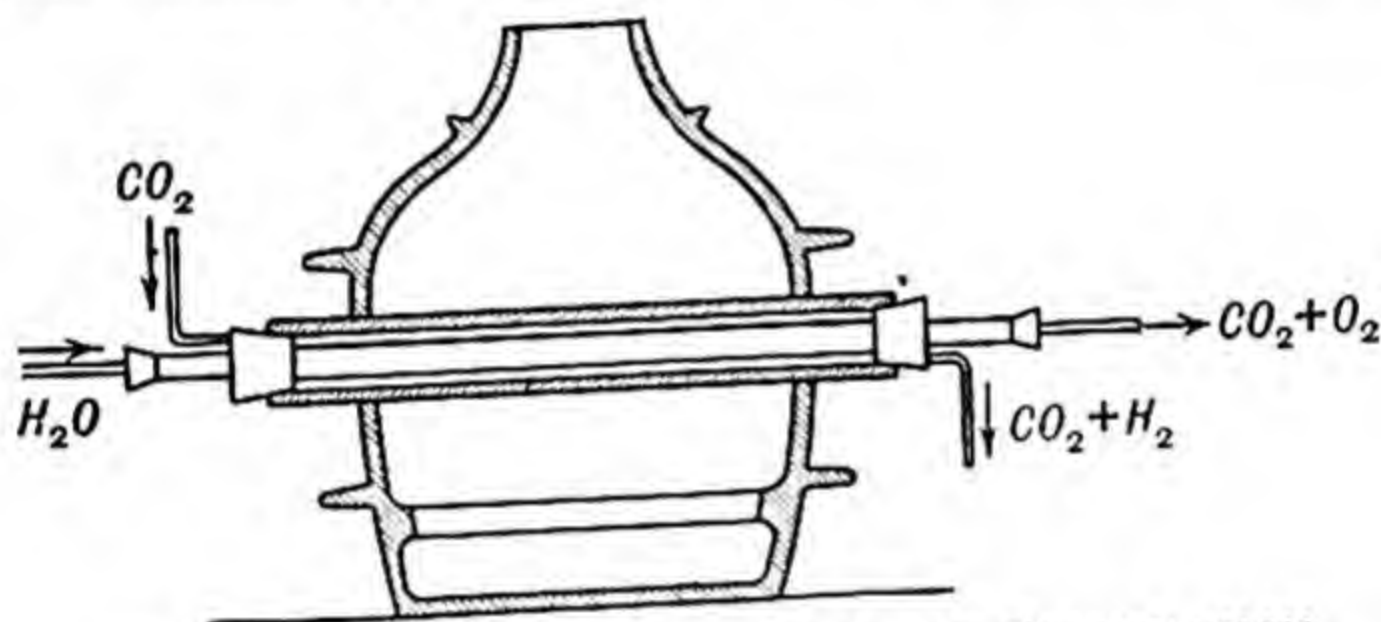
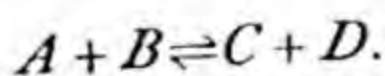


FIG. 159.—DEVILLE'S EXPERIMENT ON DISSOCIATION.

carbon dioxide through the annular space, and the gases from both were collected over potash solution, which absorbed the carbon dioxide. The steam was dissociated, and the hydrogen passed out by diffusion through the porous tube into the annular space, leaving most of the oxygen in the inner tube. This method is often called 'freezing an equilibrium.'

**\*Equilibrium and speed of reaction.**—The effect of increasing the *concentration* of a substance is to increase the velocity of the reaction which uses up that substance, and since this applies to *each* substance taking part in the reaction, *the velocity of reaction will be proportional to the product of the concentrations of the reacting substances.*

Consider two substances *A* and *B* which react to produce two other substances *C* and *D*, the latter in turn reacting to produce *A* and *B* by the reversed reaction, so that a *state of equilibrium* is set up :



Suppose that *A* and *B* are each initially present in a concentration of 1 mol per litre. In Fig. 160 the reaction  $A + B \rightarrow C + D$

*begins* with a velocity represented by  $OM$ . As the reaction proceeds two things happen :

(i) The concentrations of  $A$  and  $B$  decrease, hence the reaction  $A + B \rightarrow C + D$  becomes progressively slower, as shown by the curve  $MSP$ .

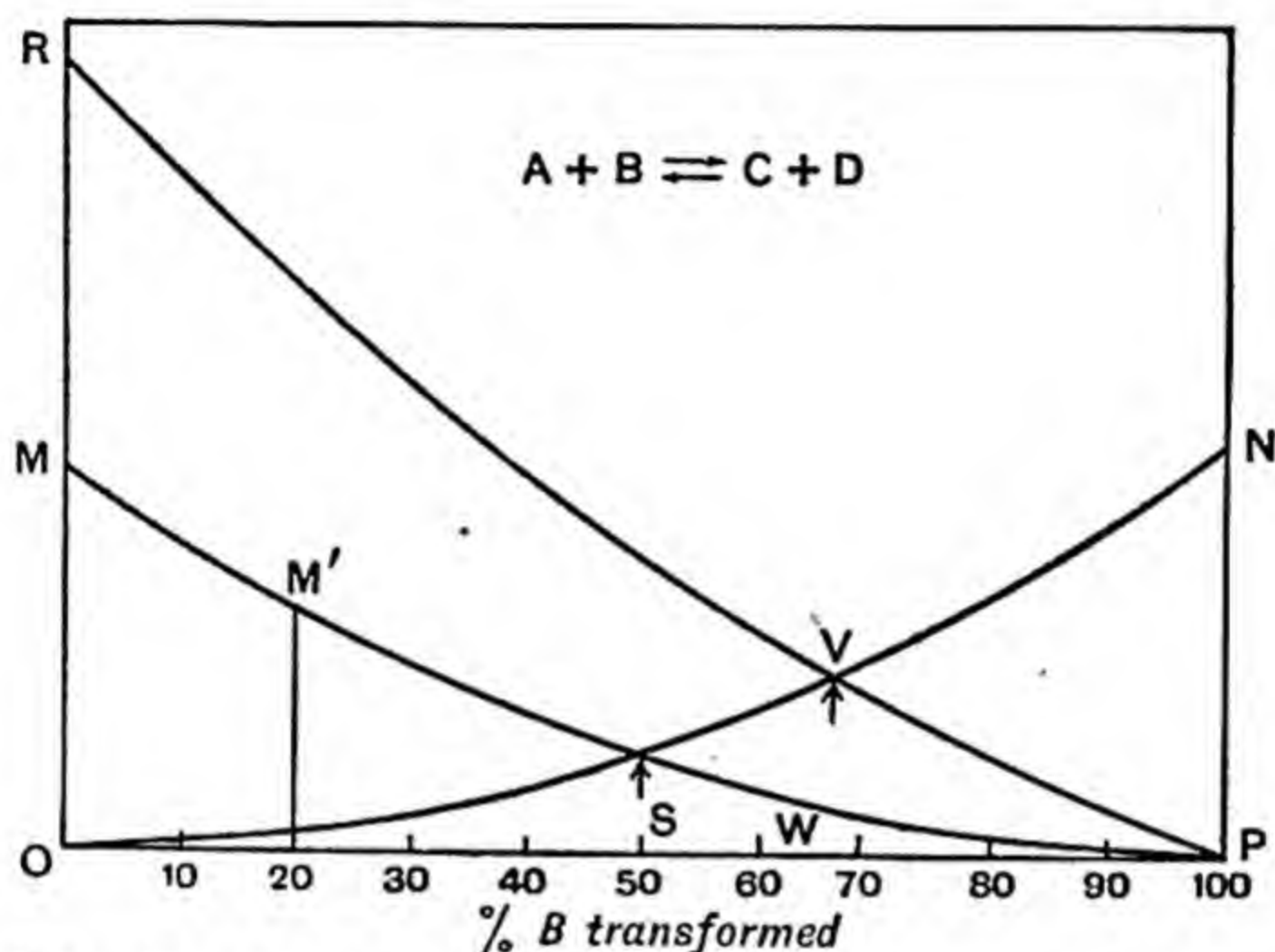


FIG. 160.—DIAGRAM ILLUSTRATING THE ATTAINMENT OF EQUILIBRIUM AND THE ACTION OF MASS. (After Prof. Deming.)

(ii) The substances  $C$  and  $D$  produced by the reaction at once begin to react so as to reproduce  $A$  and  $B$  again, at first only very slowly, since  $C$  and  $D$  are at first present only in small amounts, but as time goes on and more and more  $C$  and  $D$  are formed, the reverse reaction increases in velocity, as represented by the curve  $OSN$ .

It is assumed for the sake of simplicity that the direct and reverse reactions proceed with equal speeds when the products of the concentrations are equal.

After a certain time the two curves will cut at a point  $S$ . The direct and reverse reactions are now proceeding equally fast, and a *state of equilibrium* is reached.

With an initial mixture of  $C$  and  $D$  the reaction  $C + D \rightarrow A + B$  commences with a velocity  $PN$ , which gradually falls off along the curve  $NSO$  as  $C$  and  $D$  are used up. The reverse reaction  $A + B \rightarrow C + D$  begins slowly at  $P$ , its velocity increasing along the curve  $PSM$  as  $A$  and  $B$  accumulate. The two curves cut



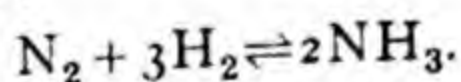
again at  $S$ , representing the same state of equilibrium as before : the equilibrium state is independent of the direction in which it is approached.

If the initial concentration of  $A$  is doubled, the forward reaction starts off with double the velocity, at  $R$ , and diminishes more steeply along the curve  $RVP$ . The velocity of the reverse reaction, however, is not changed by increased concentration of  $A$  and is again given by the curve  $OVN$ . The two curves cut at the point  $V$ , which represents a new state of equilibrium, and since  $V$  lies to the right of  $S$ , more of  $C$  and  $D$  are present in equilibrium, a result in accordance with the law of mass action. It must be carefully noted that doubling the concentration of  $A$  does *not* double the amount of  $B$  transformed when equilibrium is reached, but only increases it. In the particular example chosen the amount increases from 50 per cent. to 67 per cent.

**\*Effect of temperature and pressure on equilibrium.**—Equilibrium states are generally disturbed by alterations of temperature and pressure and new equilibrium states result. The direction of change is given by a very general law enunciated by Le Chatelier, called the law of reaction : *when a system in equilibrium is disturbed, a change takes place in the system which tends to diminish the action of the disturbing cause.*

One example is the action of mass (p. 223) : when the concentration of a substance is increased a reaction occurs which uses up some of the substance.

Now consider a system in equilibrium composed of ammonia, nitrogen and hydrogen :



Let the *pressure* be increased. A reaction will occur which tends to diminish the pressure, *i.e.*, more nitrogen and hydrogen combine to form ammonia, since this takes place with diminution in volume (4 volumes produce 2 volumes). If the pressure is decreased, ammonia decomposes.

Now let the *temperature* be increased. A reaction will occur which tends to diminish the temperature, *i.e.*, some ammonia will decompose, since this is a reaction which absorbs heat, ammonia being an **exothermic** compound, formed from its elements with evolution of heat. If the temperature is decreased, ammonia is formed.

It is important to notice that *the law applies only to systems in equilibrium*. When gunpowder is heated, so far from a

reaction taking place which tends to lower the temperature, the whole mass explodes with a great resulting rise in temperature. Gunpowder is not a system in equilibrium, and the law does not apply to it.

It is also necessary carefully to distinguish between the effect of temperature on *equilibrium* and on *velocity of reaction*. In

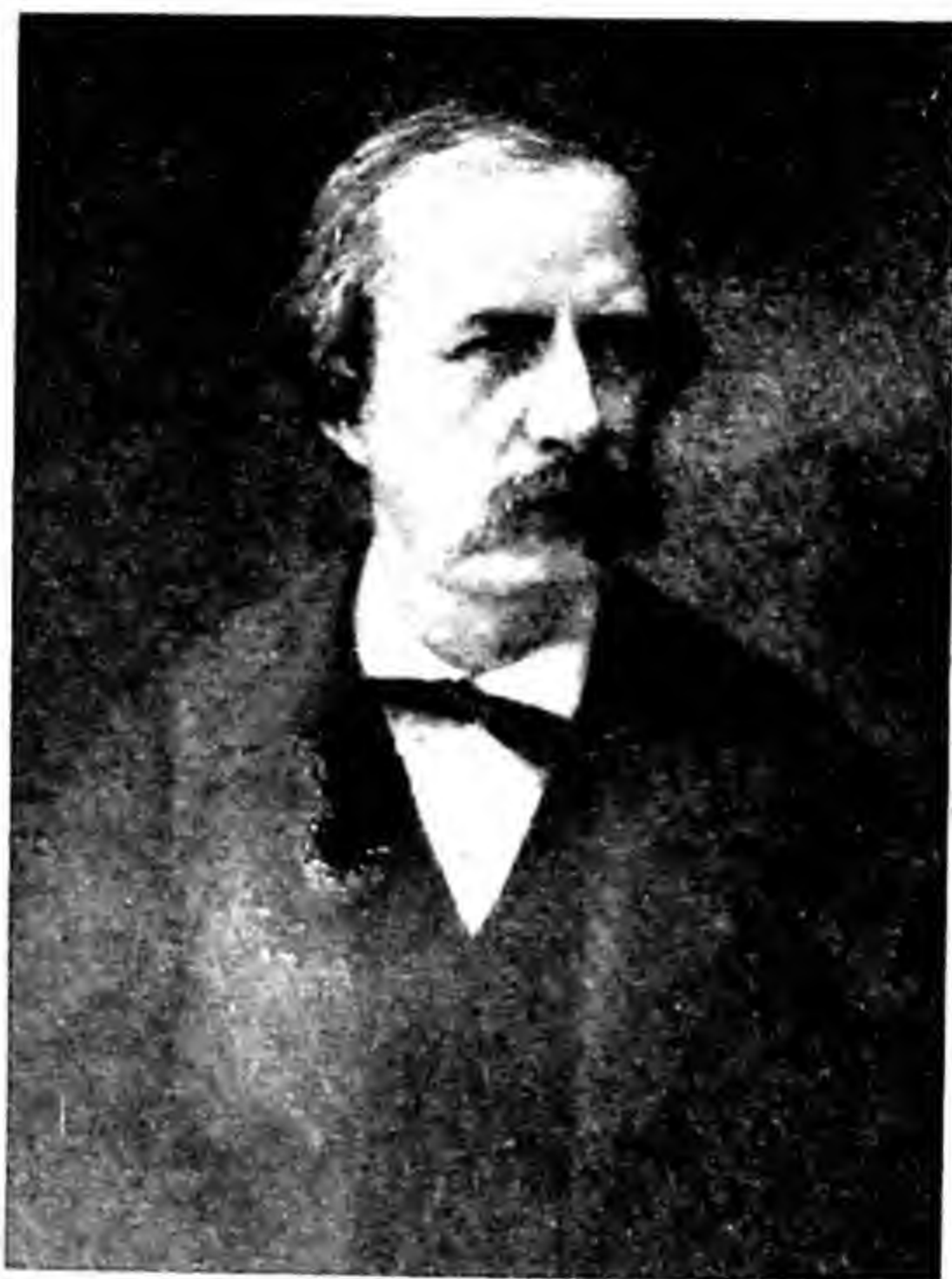


FIG. 101. MAURICE BERTHELOT, 1827-1907.

the very reverse case the reaction  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$  is one) *the velocity of reaction increases markedly with rise in temperature*. When nitrogen and hydrogen in presence of iron (which increases the velocity of reaction, or acts as a catalyst) are gradually heated from room temperature, no appreciable amount of ammonia is produced until the temperature reaches a certain value, since the velocity of formation



of ammonia is very small at the lower temperatures. The amount of ammonia formed *in equilibrium* is, however, less the higher the temperature. In practice such a temperature is used as leads to an appreciable velocity of formation of ammonia but is yet not so high as to diminish seriously the equilibrium yield of that substance, as, for example, in the Haber process



FIG. 102. -WALTHER NERNST.

for the manufacture of ammonia (see p. 379). A compromise has to be made, since the effect of rise of temperature is favourable to one condition (reaction velocity) but unfavourable to the other (equilibrium yield).

\* **Affinity and heat of reaction.** -It was formerly assumed that chemical combination was due to forces of attraction between the reacting particles, these forces being called **affinity**. The

work done by these forces would reappear in some other form of energy when the reaction was completed, and Berthelot was of the opinion that the *heat evolved* in the reaction was a measure of the affinity. It was afterwards shown by Helmholtz that a better measure of the affinity is the *utilisable* energy (free energy) which can be obtained from a reaction, say by allowing it to proceed in a voltaic cell and so producing electrical energy (p. 214). Heat energy at a constant temperature cannot be utilised in performing work, since every heat engine requires two different temperatures, a higher temperature for the boiler, or place where heat is taken in, and a lower one for the condenser, or place where heat is rejected.

Heat energy resides in molecular motions, and at very low temperatures the quantum theory sets a limit to these (p. 190). At very low temperatures the heat set free in a reaction may be taken as the equivalent of the work done by the forces of attraction, since practically no heat will reside in the substance in the form of molecular motions. This principle, due to Nernst, enables the equilibrium state in a given reaction to be more or less anticipated and computed, and is of great importance in chemical industry.



## CHAPTER XV

### THE PERIODIC LAW AND ATOMIC STRUCTURE

**The periodic system of the elements.**—The most satisfactory system of classification of the chemical elements, and the one now adopted, is based on *the relation between the properties of the elements and their atomic weights*.

So early as 1817, Döbereiner noticed regularities in the atomic weights of elements which were chemically analogous. In groups of three such elements, the atomic weight of the middle element is approximately the mean of the atomic weights of the extreme elements. This is known as the **law of triads**. Thus in the following groups this is observed :

$$\frac{\text{Cl}35.5 + \text{I}127}{2} = 81 (\text{Br} = 80) : \text{chlorine, bromine and iodine ;}$$

$$\frac{\text{S}32 + \text{Te}128}{2} = 80 (\text{Se} = 79) : \text{sulphur, selenium and tellurium.}$$

Newlands, in 1863, observed that if the elements are arranged in *the order of atomic weights*, 'the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music.' He called this the **law of octaves**.

1 H	2 Li	3 Be	4 B	5 C	6 N	7 O
8 F	9 Na	10 Mg	11 Al	12 Si	13 P	14 S
15 Cl	16 K	17 Ca	18 Cr	19 Ti	20 Mn	21 Fe, etc.

This relationship, which is based on what are now called the **atomic numbers** of the elements, was not wholly satisfactory, as can be seen, since manganese, for example, does not resemble phosphorus, yet Newlands' table contained the germ of the **Periodic System of the Elements**, put forward almost simultaneously in 1869-70 by Mendeléeff in Russia and by Lothar Meyer in Germany.

In recent years this has acquired supreme importance.

The essence of the Periodic Law is contained in Mendeléeff's statement, that 'the properties of the elements are in periodic dependence upon their atomic weights.'



FIG. 103.—DMITRI IVANOVITCH MENDELÉEFF, 1834-1907.

The content of the periodic law is elucidated by forming the periodic table, exhibiting all the elements arranged according to their atomic weights.

The Periodic Table is drawn up as follows. The elements, starting with hydrogen, are first arranged in ascending order of their atomic weights. In this continuous sequence it is found that similar, or chemically related, elements *recur at regular intervals*, so that the series is broken up into a number of **periods**,





The inactive gases (Group O or VIII *b*) form no compounds and have zero valency. The hydrogen valency increases from 1 (*e.g.*, in LiH) till group IV is reached, when it is 4 (*e.g.*, in CH<sub>4</sub>) and then diminishes from 4 to 1 (*e.g.*, in HF). The oxygen valency, however, increases steadily from 1 to 7, and in Group VIII *a* it reaches the value 8.

**The elements in the periodic table.**—The periodic table (p. 235) begins with hydrogen in Group I, which, with helium in Group VIII *b*, forms the first period. The numbers, giving the order of occurrence in the table, are the **atomic numbers**. The second period begins with the alkali metal lithium and contains eight elements, ending with the inert gas neon, which resembles helium. The third period begins with the alkali metal sodium and ends with the inert gas argon. The elements in corresponding groups (*e.g.*, Li, Na ; C, Si ; N, P ; F, Cl ; Ne, A) resemble one another. A fourth period begins with the alkali metal potassium and proceeds normally as far as manganese, which is a metal but resembles chlorine in some of the compounds in which each element has higher valencies, *e.g.*, KClO<sub>4</sub> and KMnO<sub>4</sub> are isomorphous. After manganese we should expect an inert gas, but instead come three elements, iron, cobalt and nickel, with atomic weights very close together, taking the place of a single inert gas element, and forming a separate group (Group VIII *a*) not so far represented. These three elements are called **transitional elements**. In the two preceding periods the strongly electronegative halogen element is separated from the strongly electropositive alkali metal by an inert gas element. In the fourth period manganese and copper, separated by the transitional elements, do not show very marked negative and positive characteristics. The fourth period proceeds until krypton, an inert gas resembling argon, is reached, and contains altogether eighteen elements. The whole period of 18 elements is regarded as forming a **long period** instead of two **short periods** of 8 elements each, as in those which precede it. The long period is divided into two **series**.

Another long period begins with rubidium, is divided by the transitional elements ruthenium, rhodium and palladium, and ends with xenon. There is another long period beginning with the alkali metal caesium, and ending with the radioactive emanation, an inert gas element (the last element in Group VII being unknown). The table ends with an incomplete period containing **radioactive elements**.



If the atomic weights are inserted, it is found that argon and potassium, and tellurium and iodine, are in the wrong order :

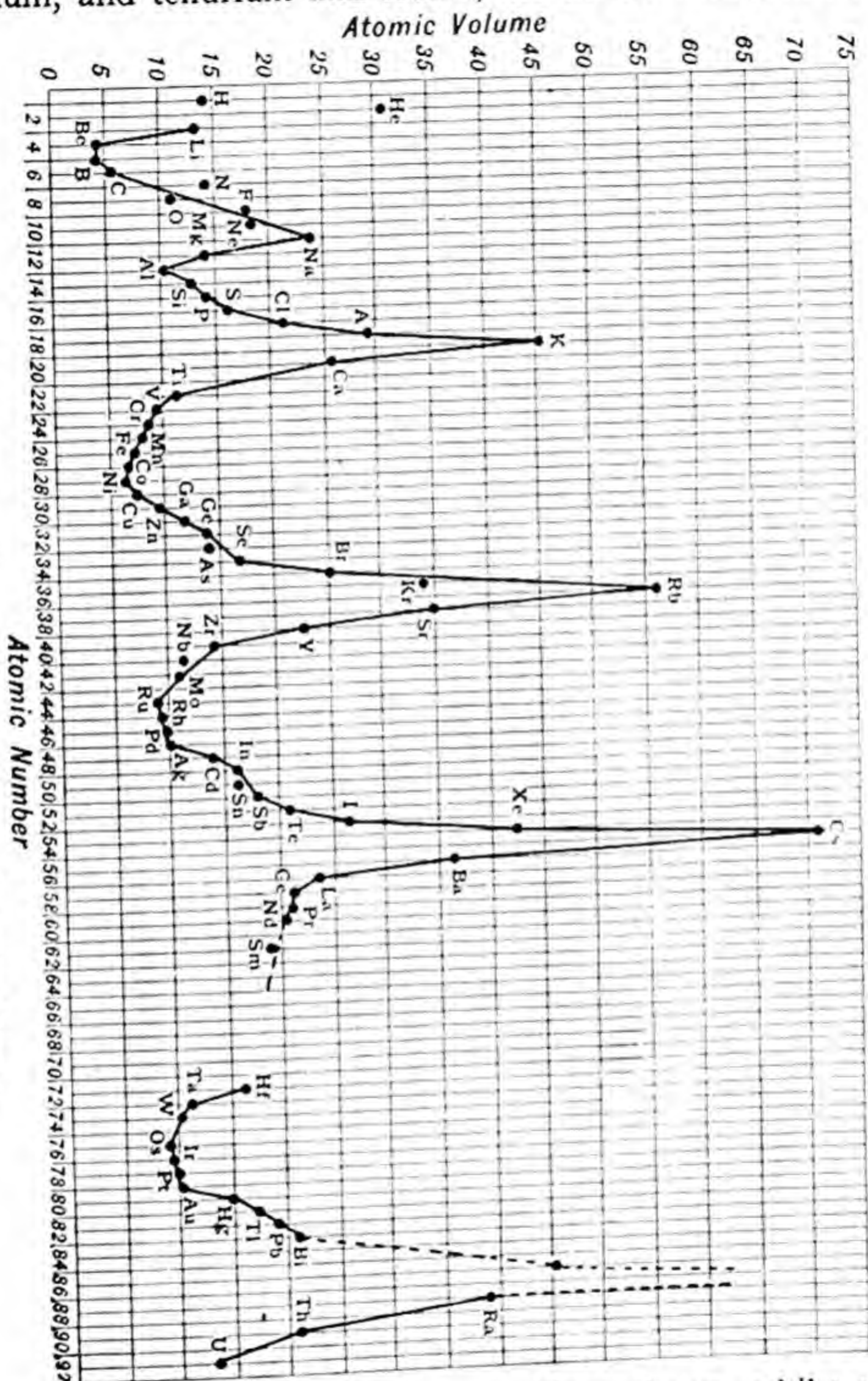


FIG. 164.—LOTHAR MEYER'S ATOMIC VOLUME CURVE.

THE ATOMIC VOLUMES OF THE ELEMENTS ARE PLOTTED AGAINST THE ATOMIC NUMBERS.

their properties place them in the positions shown, whilst the order of atomic weights would place potassium (39) before argon (40), and iodine (127) before tellurium (127.5). This is

an anomaly, which has been explained by the discovery (p. 245) that most elements are mixtures of **isotopes** with different atomic weights. Some gaps in Mendeléeff's original table were filled by elements later discovered, *e.g.*, a vacant space in Group VII by the element rhenium (Re), discovered in 1925 by Noddack,



FIG. 125.—SIR J. J. THOMSON.

Evans and Berg in platinum ores, and since found in ores of niobium (which is an element of Group VI).

A difficulty in the table is the position of the elements of the rare earths, a group of fifteen elements (including one missing recently) which follow barium. They resemble one another very closely in their properties and cannot, therefore, be placed in different groups. They are put in one place in the table, as shown, and after them comes a newly discovered element, hafnium, which belongs to Group IV. It was discovered by



Coster and Hevesy in 1923 in zirconium minerals. It will be seen that nearly all the places have been filled and that only one or two elements remain to be discovered (see p. 245).

**Atomic volume curve.**—The periodicity in properties of the elements is strikingly shown in the **atomic volume curve** (Fig. 164), due to Lothar Meyer, in which atomic volumes (volumes in c.c. occupied by the atomic weight in grams = at. wt. divided by density) are plotted against the atomic numbers, *i.e.* the ordinal numbers of the elements in the periodic table on p. 235.

The atomic volumes rise and fall in a periodic manner, following the periodic table. The alkali metals, the atoms of which are unusually bulky, are at the peaks of the curve.

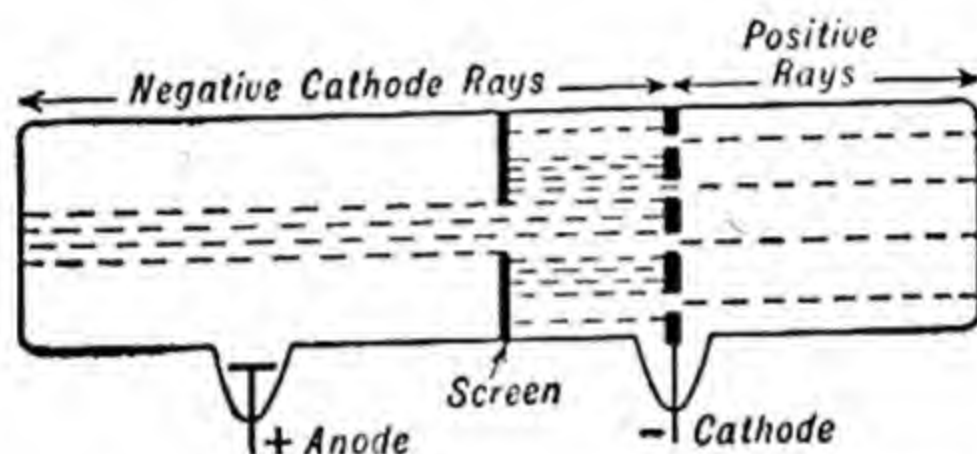


FIG. 166.—ELECTRIC DISCHARGE IN A GAS AT LOW PRESSURE.

**Utility of the periodic table.**—The periodic table has several advantages over any other system which has been proposed for the classification of the elements :

1. It enables the elements to be classified in a very simple manner, since only the atomic weights are required in order to place the elements in the table.
2. It includes in itself some previous methods of classification, such as that according to valency.
3. It enables the atomic weight of an element to be checked, since if the wrong multiple of the equivalent had been taken, there would have been no place in the table for the element: Mendeléef was able to correct several atomic weights in this way.
4. The existence of empty spaces in the table directs attention to undiscovered elements, and also, from the position in the table enables the properties of these elements to be predicted. Mendeléeff in this way predicted the existence of two or three elements which were afterwards discovered and found to have the properties he predicted for them.
5. The periodic table is closely related to much of our new

information on the structure of the atom and has proved of great service in this field. It is undoubtedly based on a fundamental law relating to the building up of atoms from their simpler ultimate components, common to all atoms.

**Isotopes.**—If an anode and cathode (p. 201) are sealed into a glass tube, and the air pumped out, it is found that at low pressure

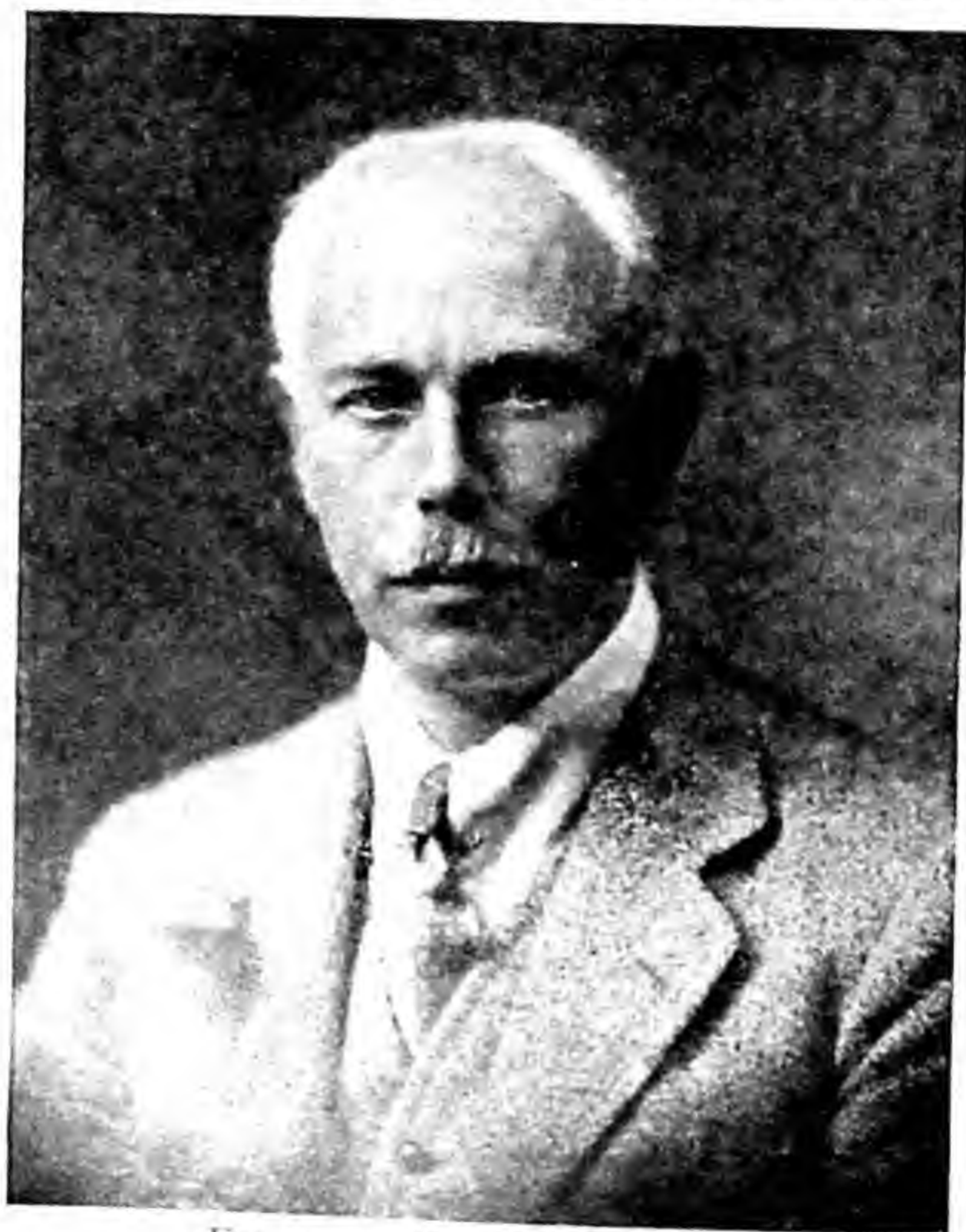


FIG. 165. DR. F. W. ASTON.  
(Phot. J. Palmer Clarke.)

a blue glow proceeds from the cathode, producing a green fluorescence where it strikes the walls of the tube (Fig. 166). This blue glow, called cathode rays, was shown by Sir J. J. Thomson to consist of negatively charged electrons, each having a mass  $1/1845$  that of the hydrogen atom, moving with high speeds. They were formed with electrodes of different materials and with different gases in the tube and therefore appear to be a common constituent of all atoms.



Goldstein and also Thomson detected in the cathode ray tube, besides free electrons, **positive rays** (formerly called **canal rays**, because they pass backwards through small apertures in the metal cathode), but none with a mass smaller than that of a hydrogen atom. The positively charged hydrogen atom is the proton (p. 205). An improved apparatus devised by Aston is shown in Fig. 168. Positive rays produced by an electrical discharge in the gas in the bulb *B* pass through the perforated cathode *C* (the anode is *A*) and then through slits *S*<sub>1</sub>, *S*<sub>2</sub>. The rays then pass through the electric field of a plate condenser, *J*<sub>1</sub>, *J*<sub>2</sub>, by which they are deflected downwards, and a fairly narrow pencil goes through a diaphragm (not shown) near the stopcock *L*. The rays then go through a magnetic field at right angles to the

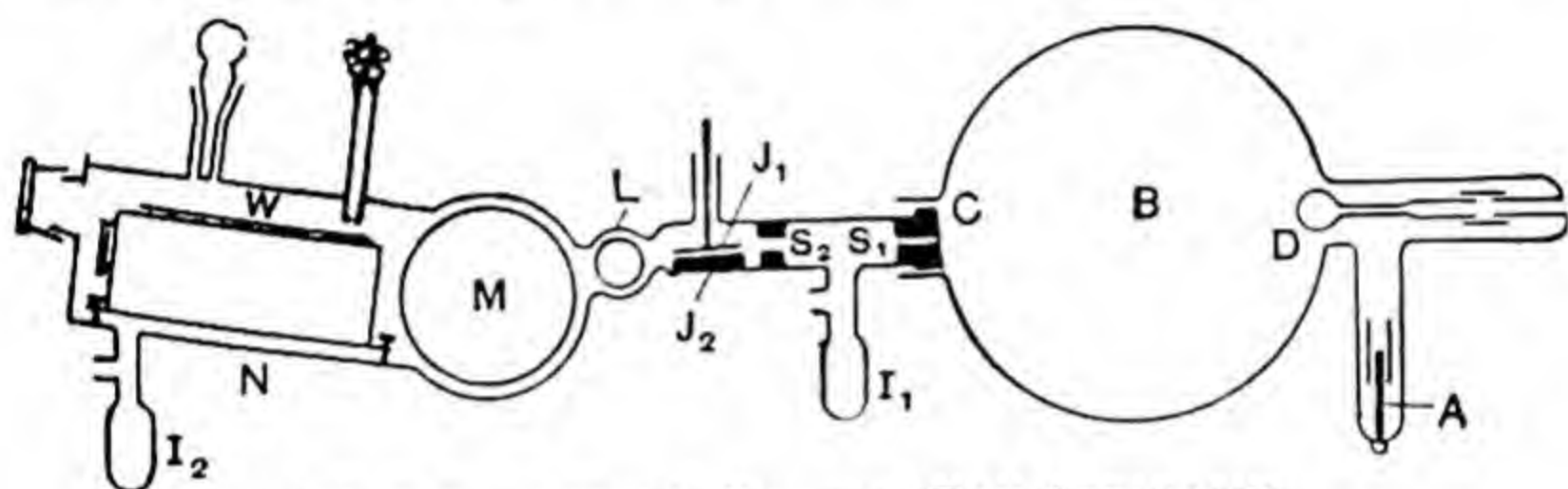


FIG. 168.—ASTON'S POSITIVE RAY APPARATUS.

electric field and to the plane of the paper at *M* (a section of a magnet pole), so arranged that the downward deflection due to the electric field is compensated. They then reach a focus on the photographic plate *W* in the camera *N*, producing a line which can be developed. A low pressure is maintained in the part of the apparatus to the left of the bulb by means of pumps and the charcoal bulbs, *I*<sub>1</sub> and *I*<sub>2</sub>, cooled in liquid air. *D* is a silica bulb which protects the opposite side of the glass bulb *B* from being melted by the intense beam of cathode rays emitted by *C*.

The rays corresponding with particles having fixed values of *mass/charge* ( $m/e$ ) produce a line on the photographic plate, resembling a spectrum line, hence the whole apparatus is called a **mass spectrograph**, the set of lines being called a **mass spectrum**. From this spectrum it is possible to calculate the values of  $m/e$  for the particles, and hence (if the charges are known) to compare the masses of various particles forming the positive rays. A set of mass spectra is shown in Fig. 169.

As a result it is found that many common elements contain atoms of different masses. In the case of chlorine, for example,

there is no line corresponding with the chemical atomic weight 35.5, but two lines corresponding with masses 35 and 37 (together with lines 36 and 38, corresponding with the two hydrogen

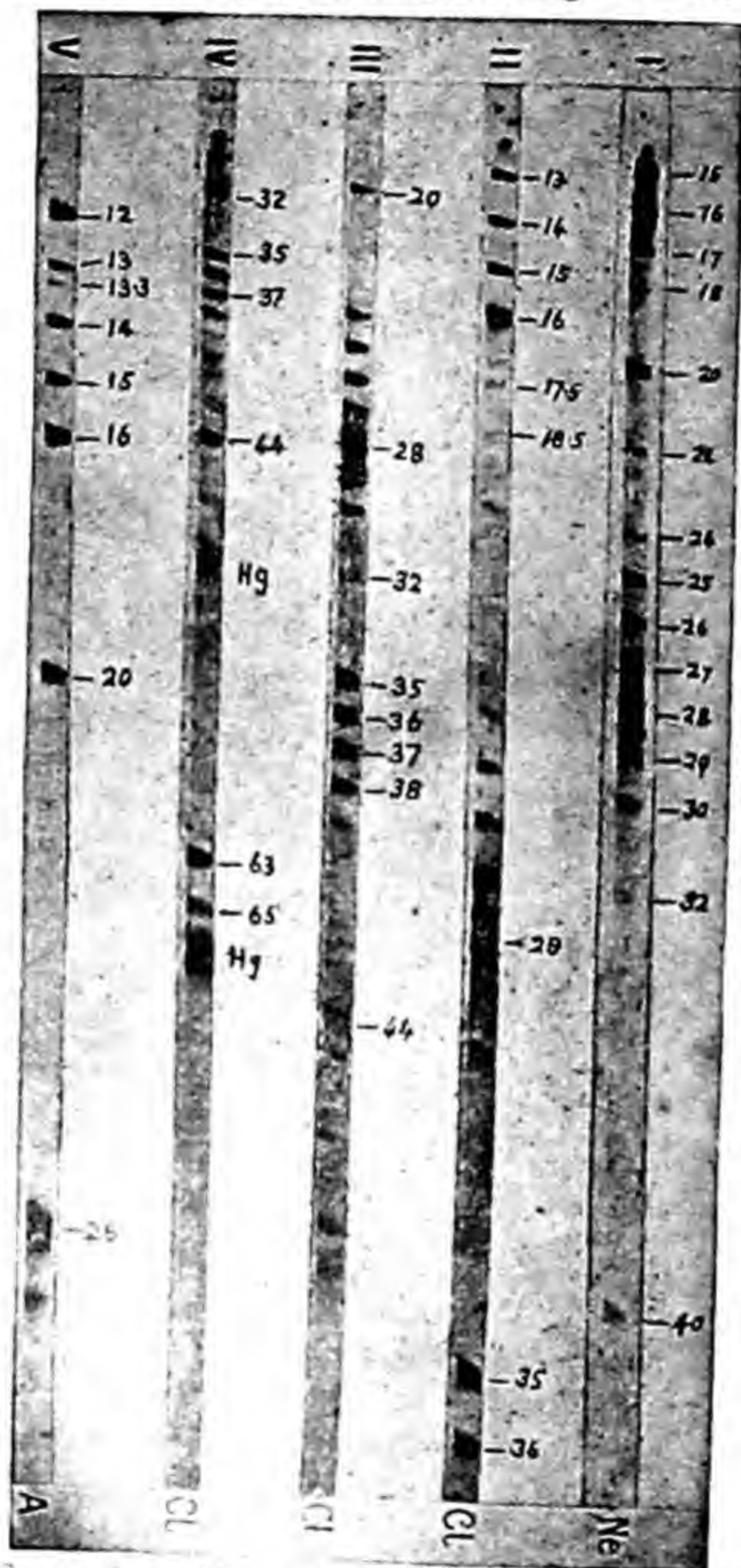


FIG. 169.—MASS SPECTRA (ASTON, 1921).

The lines additional to those of the isotopes of the elements indicated are due to impurities in the discharge tube.

chlorides). Ordinary chlorine is a mixture of the two varieties of chlorine, its mean atomic weight being 35.5. Since no variation in the atomic weight of chlorine has been found, the two



varieties must always be found mixed in the same ratio. Such varieties of an element are called **isotopes** (p. 126); ordinary chlorine is a mixture of the two isotopes of chlorine of masses 35 and 37. Many other elements besides chlorine are found to be mixtures of isotopes, *e.g.* carbon of isotopes of masses 12 and 13, nitrogen of isotopes 14 and 15, oxygen of isotopes 16, 17 and 18,



FIG. 170. H. G. J. MOSELEY.  
(Photo by W. H. Hayles.)

potassium of isotopes 39, 40 and 41, etc. The name isotope (from the Greek *isos*, equal, and *topos*, place) denotes that *each place in the periodic table may contain two or more isotopes forming together what was formerly regarded as a single element*. Thus, the place occupied by chlorine includes the two isotopes of chlorine, 35 and 37.

Hydrogen also contains isotopes, *viz.* ordinary hydrogen of mass 1 and the so-called 'heavy hydrogen' or **deuterium** of

mass 2, discovered in 1932 by Urey, Brickwedde and Murphy, and denoted by the symbol D. Ordinary water

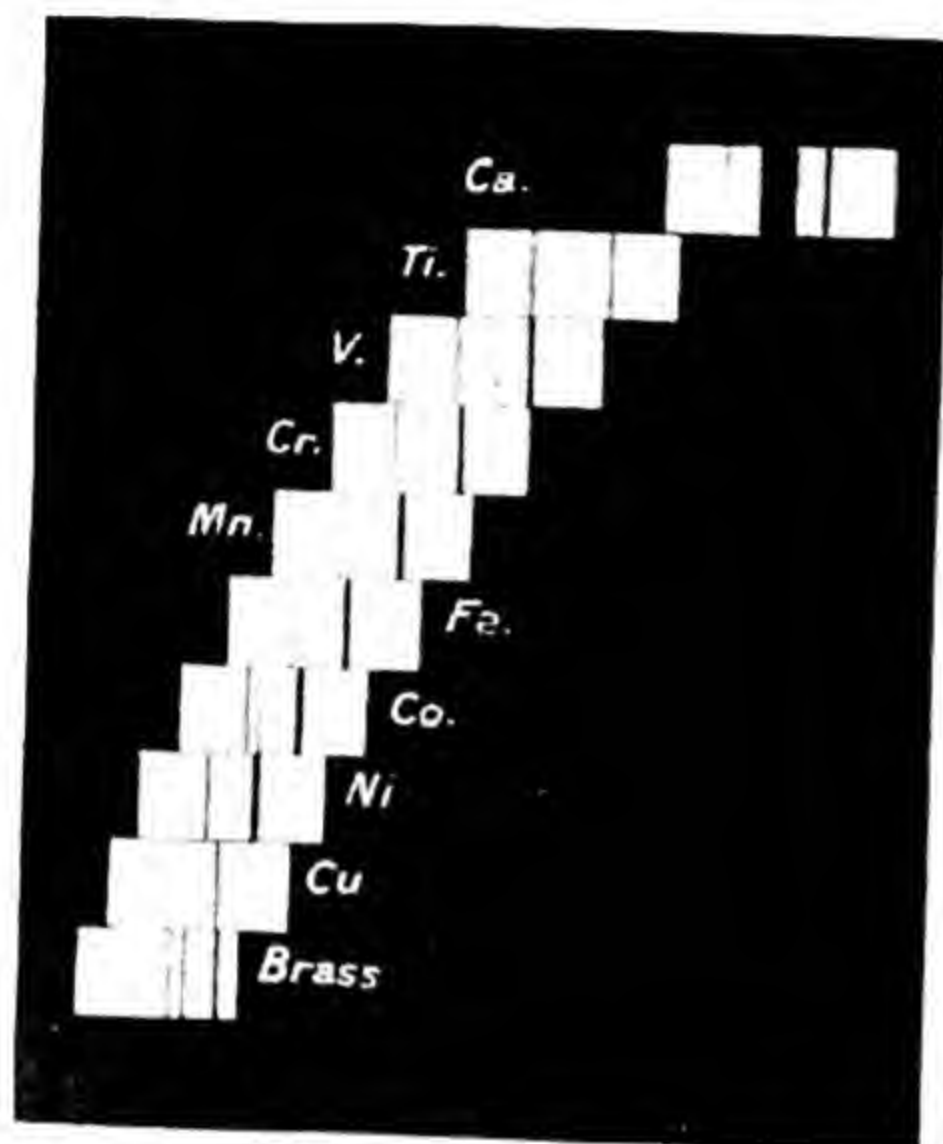


FIG. 121. X-RAY SPECTRA (Moseley)  
K-RAYS.

cal or chemical means, the properties of hydrogen and deuterium differ sufficiently to allow of separation, say by diffusion.

**Atomic numbers.**—A discovery of fundamental importance was made in 1913-14 by Moseley, working in Manchester and Oxford. Moseley was unfortunately killed at Gallipoli in the Great War. His work was based on the discovery by Barkla and by Kaye that each solid element, when bombarded by cathode rays in a vacuum tube emits X-rays of definite wave-length characteristic of that element. These rays may be refracted by crystals, acting like diffraction gratings for ordinary light, and hence may be separated into a spectrum. In this way the wave-lengths of the X-rays can be found. The velocity of light divided by the wave-length gives the frequency. Various types of rays are emitted, but one type, the so-called K-rays, appeared to give two lines (really consisting of two pairs of two lines, very close together), as shown in Fig. 121. In this, the spectra are placed approximately in order, parts representing the same

contains about 1 part in 6000 of the oxide of deuterium,  $D_2O$ , or 'heavy water,' which can be isolated in the pure state. Deuterium oxide has a density of 1.1, freezes at  $+3.8^\circ$  and boils at  $101.4^\circ$ . A third isotope of hydrogen, of mass 3 (tritium), is produced artificially by the collision of deuterium nuclei (p. 256). Although the chemical and physical properties of all the other isotopic elements are so nearly alike that the elements can scarcely be separated into their isotopes by ordinary physi-



angle of refraction by the crystal being in the same vertical line. In 1914 Moseley showed that the square roots of the K-frequencies when plotted against the atomic numbers, *i.e.* the ordinal numbers of the positions of the elements in the periodic table (p. 235) give straight lines. He suggested that *the atomic number is equal to the positive charge on the nucleus of the atom*, the electronic charge being the unit.

Moseley's method obviously provides a method of determining the atomic number from the wave-length of the X-rays emitted by an element, and so enables the position of an element in the periodic table to be fixed. Tellurium and iodine, for example, have atomic numbers of 52 and 53, in the order expected from their chemical properties, whilst their atomic weights place them in the opposite order. Since most elements are mixtures of isotopes, the atomic weight is only a mean value and has not much significance. The method also indicates whether any elements are missing from the table, since if two elements have atomic numbers differing by unity no other element can come between them, whilst if their atomic numbers differ by two, another element must come in between. It was found that lutecium, the last element of the group of rare earths, had the atomic number 71, whilst the next known element of higher atomic weight, tantalum, had the atomic number 73. An unknown element of atomic number 72 must, therefore, come between lutecium and tantalum. This was sought for and discovered by Coster and Hevesy in 1923; it is the element hafnium. It was found in this way that nearly all the elements within the structure of the periodic table are known.

**The structure of the atom.**—Dalton and chemists generally throughout the nineteenth century regarded the atom as a kind of minute, hard billiard ball, incapable of division, all the atoms of a given element being exactly alike. The discovery of isotopes disproved the second assumption. Ever since Prout in 1815 suggested that all elements are formed from a single material, hydrogen, chemists also suspected that the chemical atoms might be divisible into simpler parts, though what these parts were or how the division was to be effected no one knew. With the discovery of radium by Madame Curie in 1898, and the investigation of radioactivity (see p. 253) by Rutherford and others, the possibility of exploring the inner structure of the atom was realised.

The modern theory of atomic structure is due mainly to Lord Rutherford. The atom of hydrogen is pictured as consisting of

a very small positively charged **nucleus**, outside which, and at a considerable distance from it, is a negative electron which neutralises the opposite charge of the nucleus. The nucleus of the hydrogen atom is the **proton** (p. 205). A still simpler atom



*(Russell, London.)*

FIG. 172. LORD RUTHERFORD.

consists of an uncharged particle, called the **neutron**, of the same mass as the hydrogen nucleus. The nuclei of atoms heavier than hydrogen are supposed to be made up of protons and neutrons; the number of protons is equal to the positive charge of the nucleus, which is equal to the atomic number, and the sum of the protons and neutrons corresponds with the atomic mass. Equal to the number of protons are as many electrons as there are protons in the nucleus. Since isotopes have the same atomic number, their nuclei have the same number of protons but different numbers of neutrons. Chlorine, with the atomic number 17, has 17 protons in the nucleus. The isotope of mass 35 has, therefore, 18



neutrons in its nucleus ( $17 + 18 = 35$ ), whilst that of mass 37 has 20 neutrons.

According to Rutherford's theory, the outer electrons revolve about the nucleus of the atom like planets round the central sun. Bohr (1913) supposed that each electron revolves in its orbit without loss of energy by radiation, but in passing from one orbit to another a quantum of energy (p. 190) is emitted, corresponding with a definite spectrum line. In this way the origin of spectra is explained and a knowledge of atomic structure may be obtained from spectra.

The atom next to hydrogen, helium, is supposed to have a nucleus of mass 4 and charge 2, composed of two protons and two neutrons. Around this nucleus revolve two electrons. Aston says: "if in the atom of helium we take the nucleus as represented by a rather large pea, its planetary electrons may be represented as two rather smaller peas revolving around it at a distance of a quarter of a mile." In still heavier atoms the two electrons of the helium atom are retained in an inner shell, next to the nucleus, and successive atoms in the periodic table may be supposed to be constituted as follows.

The positive charge of the nucleus increases by 1 unit for each successive step in atomic number. The mass of the nucleus increases, usually by more than 1 unit, by addition of protons and neutrons. The mass is the total number of protons and neutrons; the atomic number is the sum of the number of protons; and the total number of outer electrons is also equal to the atomic number. The structures of the atoms from hydrogen to neon can then be represented as follows:

	<i>Mass of nucleus.</i>	<i>Atomic number = charge on nucleus.</i>	<i>Electrons.</i>
H	1	1	1
He	4	2	2
Li	7	3	2 + 1
Be	9	4	2 + 2
B	11	5	2 + 3
C	12	6	2 + 4
N	14	7	2 + 5
O	16	8	2 + 6
F	19	9	2 + 7
Ne	20	10	2 + 8

When a 2-electron shell is completed with helium, a new shell begins to be formed, containing from 1 electron in lithium to

8 electrons in neon. The structures of the next period of atoms higher than neon (p. 235) is a repetition of this, a new shell of 8 electrons being completed with the next inert gas, argon. The outer shells of inert gases contain 8 electrons, and this stable



*(Century Co., N.Y.)*

Fig. 173. G. N. Lewis

arranging of an outer shell of 8 electrons suggests an arrangement at the corners of a cube (Fig. 2, Lewis, 1918). In Fig. 174 the inner shells are supposed to be contained inside the cubes, only the outer electrons being shown.

The light elements of periods 2 and 3 (p. 235) correspond with steps 1 and 2, or with one or two successive shells of 8 electrons around the nuclei; the positive charges of the nuclei increase in steps of 1 unit from one element to the next. Periods 4 and 5



contain 18 elements each, so that it is supposed that shells of 18 electrons are completed. Since the outer shells of krypton and xenon each contain 8 electrons, there must be completed shells of  $8 + 10$  electrons below them, the original outer shell of 8

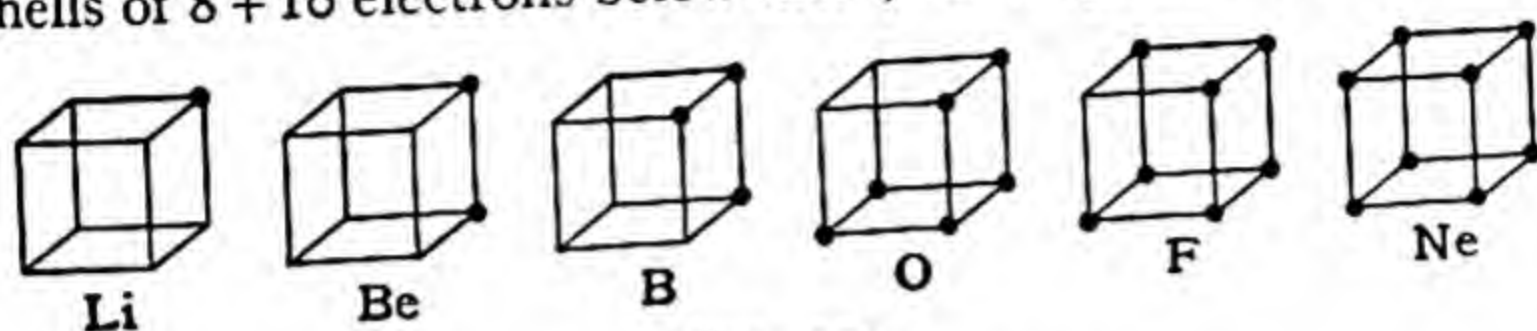


FIG. 174.

STRUCTURE OF ATOMS ON THE OCTET THEORY.

thus expanding to 18. The electronic configurations of the inert gases are, therefore :

He	-	-	2
Ne	-	-	$2 + 8$
A	-	-	$2 + 8 + 8$
Kr	-	-	$2 + 8 + 18 + 8$
Xe	-	-	$2 + 8 + 18 + 18 + 8$
Em	-	-	$2 + 8 + 18 + 32 + 18 + 8$

Period 6, if we include the missing element 85, contains 32 elements, hence 32 electrons are added in succession in passing from xenon to the emanation. In passing through the series of rare earths the *inner* group of 18 electrons of xenon expands to 32 and the *outer* group expands from 8 to 18, whilst at the same time a new outer group of 8 is built up around the inner group expanding to 18. The arrangement of electrons around the nuclei of the atoms of the elements is shown in the table on page 250. All elements having the same completed groups of electrons (2, 8, 18 or 32) are shown in the same horizontal row, the vertical columns including elements with the same number of electrons in the incomplete outer groups, shown at the top. The electronic arrangements are read off as follows :

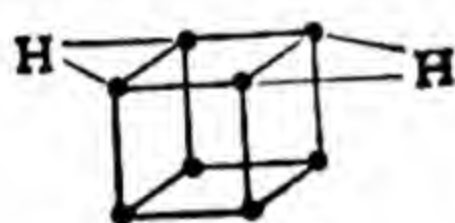


FIG. 175.  
WATER MOLECULE

$$\text{O } 2 + 6 \quad \text{Ca } 2 + 8 + 8 + 2 \quad \text{Fe } 2 + 8 + 14 + 2$$

When scandium is reached, instead of the group  $2 + 8 + 8 + 3$  being formed, the group  $2 + 8 + 8$  expands to  $2 + 8 + 9$  and 2 electrons form an outer shell. In the ion  $\text{Sc}^{+++}$  these two electrons and one from the inner group are lost, so that the ion has the same





between the ions, these being held by electrostatic attraction in the lattice (Fig. 142, p. 190), whilst in solution the ions are free.

Lewis assumes that *in the formation of an ordinary single valency bond (co-valency) a pair of electrons is shared in common by two atoms*. In this way one or both atoms complete an octet of electrons. The water molecule is formed from the oxygen atom with 6 electrons, and 2 hydrogen atoms each with 1 electron, and the oxygen in water is surrounded by 8 electrons (Fig. 175). The formation of a molecule of chlorine

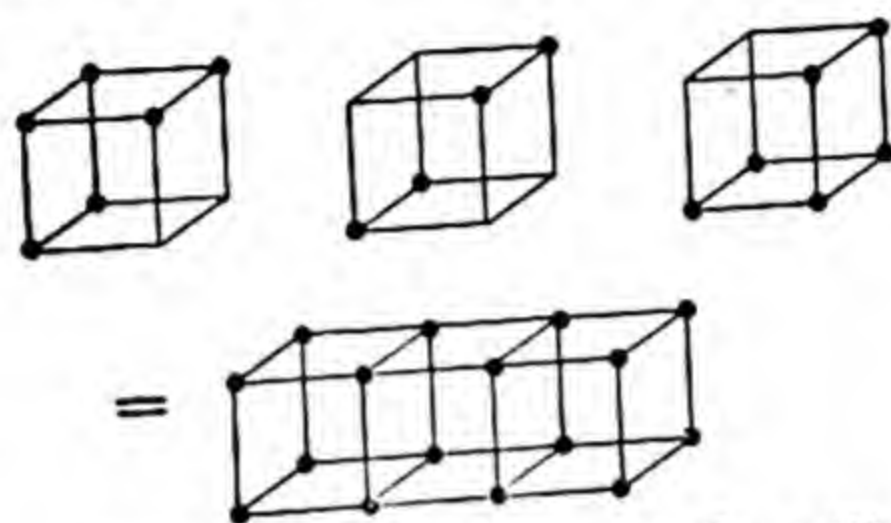


FIG. 176—FORMATION OF CARBON DIOXIDE.

from two atoms of chlorine, each with 7 electrons, may be represented by two cubes joined along an edge, this edge having a shared pair of electrons and representing the single bond. If the outer electrons are represented by dots, each atom of chlorine will be  $\cdot\ddot{\text{Cl}}\cdot$  and the chlorine molecule will be  $\cdot\ddot{\text{Cl}}:\ddot{\text{Cl}}\cdot$ , which is the electronic formula corresponding with the structural formula  $\text{Cl}-\text{Cl}$ .

A double bond is formed by *four* equally shared electrons, two from each atom. Fig. 176 shows the formation of carbon dioxide from  $\text{C} + 2\text{O} = \text{O}::\text{C}::\text{O}$ , the double bonds in  $\text{O}=\text{C}=\text{O}$  each having four electrons.

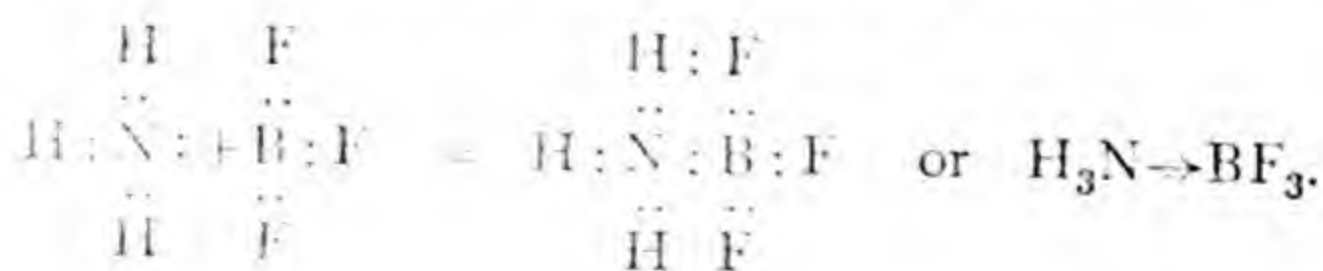
When the pair of electrons required to form a covalent link comes from *the same atom* instead of being provided by, and equally shared between, two atoms, a *co-ordinate link* is formed. Co-ordinate links are formed when apparently saturated molecules add on other molecules to form what were previously called 'molecular compounds.' Boron has 3 electrons in the outer shell and can share these with 3 fluorine atoms, forming the saturated compound  $\text{BF}_3$ , in which the boron is surrounded by

6 electrons. Nitrogen has 5 outer electrons and shares 3 with three hydrogens forming ammonia,  $\text{NH}_3$ , with an outer octet. Of this octet, 2 electrons form a *lone pair*, *i.e.* are unshared. This pair may be *donated* to the boron atom in  $\text{BF}_3$ , raising the



FIG. 177.—MADAME CURIE.

number of electrons round the boron from 6 to 8. The resulting link is denoted by an arrow instead of a line:





For this reason ammonia adds to many metallic salts, forming what are called **co-ordination compounds**, *e.g.*  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ . The number of groups co-ordinated with the metal atom is usually 4 or 6.

**Radioactivity.**—In 1896, a year after the discovery of the X-rays by Röntgen, the French physicist Becquerel noticed that compounds of **uranium** affected a photographic plate wrapped in black paper and he named the effect radioactivity. Two years later Schmidt and Madame Curie, independently, found that **thorium** compounds produce the same effect. Madame

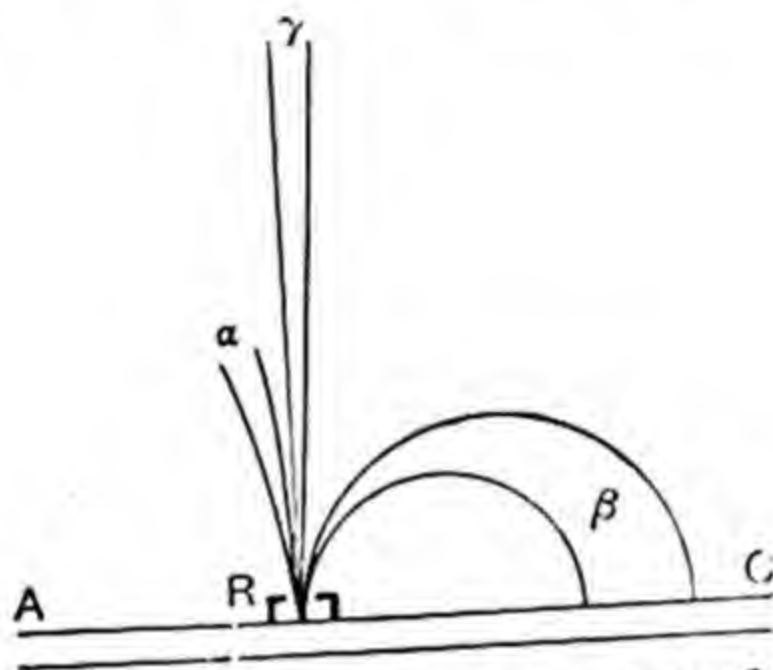


FIG. 178.—DEFLECTION OF  $\alpha$ - AND  $\beta$ -RAYS FROM RADIUM BY A MAGNETIC FIELD.

THE  $\alpha$ -RAYS HAVE A SHORTER 'RANGE' IN AIR BEFORE ABSORPTION THAN THE  $\beta$ -RAYS.

Curie then found that some uranium minerals are four times as active as pure uranium, and the presence in them of some more active substance was confirmed in 1898 by M. and Mme. Curie, who isolated from the uranium ore, pitchblende, two active bodies, one over a million times more active than uranium, which were called **polonium** (after Mme. Curie's native country) and **radium**.

Investigations of radioactive substances, particularly by Rutherford, showed that their properties are due to the emission from them of three different kinds of rays: the  $\alpha$ -rays, the  $\beta$ -rays and the  $\gamma$ -rays.

The  $\alpha$ -rays are doubly-positively charged helium atoms, *i.e.* **helium nuclei** (p. 247) emitted with great velocity, ploughing their way through the atoms of the air, knocking out some of their electrons and so making the air a conductor of electricity and causing the discharge of a gold-leaf electro-

scope. This property of imparting conductivity to gases is called *ionisation*.

When an  $\alpha$ -particle collides with a phosphorescent screen of zinc sulphide, it causes the emission of a flash of light. These flashes may be counted and so the number of  $\alpha$ -particles counted, and from this the number of molecules in 1 c.c. of helium is found, as previously explained (p. 170). This apparatus is called a *spintariscope*. The  $\alpha$ -rays also affect a photographic plate.

The positive charge of the  $\alpha$ -particles is shown by their deflection in a magnetic field.

The  $\beta$ -rays are free electrons shot off with great velocity, ionising air, affecting a photographic plate, and suffering deflection in a magnetic field in the opposite direction to  $\alpha$ -rays (Fig. 178). On account of their small size and great velocity, the  $\beta$ -rays can pass through sheets of metal.

The  $\gamma$ -rays are not corpuscular, but are X-rays of very small wave-length. They are not deflected by a magnetic field, but they ionise air by shaking the electrons out of atoms, they affect a photographic plate and are very penetrating, passing through some inches of lead.

Radium, thorium and a third radioactive element, *actinium*, but not uranium, have the property of emitting radioactive gases, formerly called the *emanations* but now named *radon*, *thoron* and *actinon*. These gases can be liquefied by dipping the tubes containing them into liquid air, they diffuse like ordinary gases, and refuse to enter into any chemical reactions, so that they belong to the inert gas group (p. 398). They differ from ordinary gases in being radioactive, emitting  $\alpha$ -particles, but rapidly lose their activity, radon losing half its initial activity in four days, thoron in less than half a minute, and actinon in a few seconds. The spontaneous production of helium from radium emanation was proved by Ramsay.

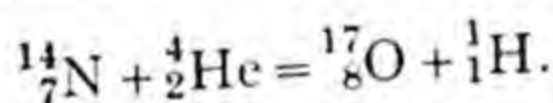
Rutherford and Soddy (1903) explained radioactive changes by assuming that atoms of radioactive elements may spontaneously break up, emitting very swift  $\alpha$ - and  $\beta$ -rays carrying large amounts of energy. In the case of radium, thorium and actinium, the first change is the emission of an  $\alpha$ -particle and the production of a gaseous emanation. This emanation in turn emits an  $\alpha$ -particle and forms a radioactive solid, which also breaks down. In the case of radium five  $\alpha$ -particles are emitted in all, and the final inactive product thus has the atomic weight  $226 - 5 \times 4 = 206$ , which corresponds with an isotope of lead. The final product from thorium has an atomic weight of



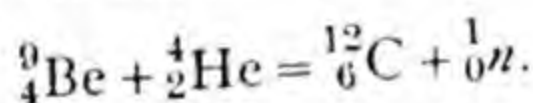
$232 - 6 \times 4 = 208$ , corresponding with another isotope of lead (see p. 126).

Each radioactive substance has a characteristic rate of decay ; the time during which half of a given number of atoms have disintegrated is called the *half-life*, and varies from a fraction of a second to thousands of years. A disintegration product of thorium, called mesothorium-I, is a by-product in the manufacture of incandescent gas mantles from monazite (p. 43). It disintegrates rather rapidly, having a half-life of  $5\frac{1}{2}$  years as compared with 1700 years for radium, but is cheaper than radium, and has been used instead of the latter in making luminous paint for watch dials.

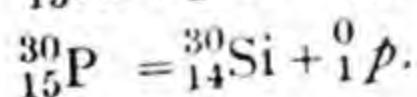
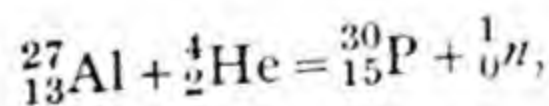
**Artificial radioactivity.**—When  $\alpha$ -rays pass through nitrogen or aluminium, protons of long range are emitted, which are supposed to come from the nucleus of the heavier element. The nucleus of an atom may be represented by the chemical symbol, the mass by an upper index and the nuclear charge by a lower index ; the above change (Rutherford, 1919) then seems to involve the formation of an isotope of oxygen :



In the bombardment of beryllium with  $\alpha$ -particles, neutrons ( ${}_0^1n$ , mass 1, charge 0) are emitted :

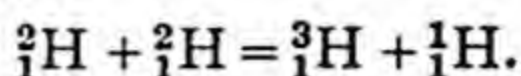


In the bombardment of aluminium with  $\alpha$ -particles, the change occurs in two stages, since the metal when removed from the rays shows radioactive properties which are due to the emission of positive electrons ( ${}_1^0p$ , charge +1, mass 0). There is first produced an isotope of phosphorus (which can be dissolved and co-precipitated with ordinary phosphoric acid) and the neutron. The phosphorus is radioactive, emits a positive electron, and forms an isotope of silicon :



High speed protons, neutrons and deuterons (heavy hydrogen nuclei) also bring about artificial transmutation of atoms which they bombard ; by the action of deuterons on sodium, radioactive sodium is prepared. By the collision of

deuterium nuclei, the heavier isotope of hydrogen tritium,  ${}^3\text{H}$  or T, of mass, 3 is formed :



In some cases, it is seen, the bombarding particle enters the nucleus of the struck particle so that elements are synthesised as well as disintegrated. This can take place when neutrons enter the uranium nucleus ; the resulting particle then emits two  $\beta$ -rays and forms two elements with atomic numbers 239 and 240, higher than the atomic number of any natural element. When the uranium isotope of mass 235, present in small amount in natural uranium, is bombarded with slow neutrons, the resulting nucleus tends to split into two nearly equal parts, with great emission of energy. The process also emits neutrons, so that in certain circumstances it can become explosive. This is the principle of the atomic bomb.



# QUESTIONS

## PART I

### INTRODUCTORY AND THEORETICAL

1. Describe the different methods that could be employed for the separation of the ingredients in a finely divided mixture of two solids. When dealing with each method (1) state the conditions under which it is applicable and (2) give one illustrative example of a pair of solids for which the method is applicable. [Madras S.L.]

2. What do you understand by an element? Describe experiments with (a) carbon, (b) chalk, to determine in each case whether it is an element or not. [Camb. Local Jun.]

3. Describe two experiments that you may have done or seen illustrating each of the following: (a) The change of an element into a compound. (b) The decomposition of a compound into its elements. [India, U.P.]

4. Explain in detail how you would determine the volume of oxygen, measured at standard temperature and pressure, which is dissolved by one litre of water at the laboratory temperature. [Madras S.L.]

5. Describe how you would separate the ingredients in each of the following, noting the properties of the ingredients which help you in separating them: (a) A gaseous mixture of about equal volumes of hydrogen, oxygen and carbon dioxide. (b) A liquid containing about equal quantities of alcohol and water. (c) A mixture of about equal quantities of common salt and nitre. [Madras S.L.]

6. Sketch the apparatus you would use in order to obtain a few c.c. of pure water from sea water. How would you find out whether the water so obtained is pure or not? Explain 'supersaturated solution' and 'water of crystallisation,' and illustrate your answer by reference to one example of each. [Joint Matric. Board.]

7. A sample of muddy water is provided. How would you find if the water contained any dissolved salt, and how would you obtain a sample of pure water from it? [India U.P.]

8. Give two examples of the use of (a) crystallisation and (b) distillation in the preparation of pure substances. [Camb. Local Jun.]

9. What is meant by (a) a saturated solution, (b) a supersaturated solution? One hundred grams of water dissolve the following weights of ammonium chloride at the temperatures named:

Temperature -	0°	10°	20°	30°	40°	50°	60°	80°	100°
Substance -	28.4	32.8	37.3	41.3	46.2	50.6	55.0	64.0	72.8 grams.

Construct the solubility curve of the substance, and from the curve determine the solubility of ammonium chloride at 24° and 70°.

[London Matric.]

10. When phosphorus is burnt in a measured volume of air a decrease of about 20 per cent. is observed in the volume of the gas. What possible conclusions can you draw from this experiment alone? Set forth carefully the further experimental grounds on which the accepted explanation of this phenomenon is based.

[Madras Inter.]

11. When copper is heated in air, a black substance is formed. How would you prove that the copper had combined with another element to form this new substance, and how could you determine what this element is?

[Joint Matric.]

12. Write an account of *one* of the following:

(a) Crystals and crystallisation.

(b) The Bunsen burner.

[Oxford and Camb. School Cert.]

13. Name the four important constituents of atmospheric air and describe simple experiments by which a specimen of each of these may be obtained from it.

[Travancore S.L.C.]

14. How would you determine the amount of water vapour in one litre of air? Give a full description of the apparatus you would use. What circumstances tend to increase or decrease the humidity of the air?

15. In what respects does the air that we breathe out differ from the air that we breathe in? Outline with diagrams a method of determining the percentage of nitrogen by volume in expired air.

16. How would you show that ordinary air contains traces of water vapour and of carbon dioxide? Sketch the apparatus that you would use to determine quantitatively the amounts of these substances present in air.

[Joint Matric. Board.]

17. Describe experiments you would perform to prove the presence of the four important constituents of atmospheric air. What important function has each of these in the economy of Nature?

[Calcutta Inter.]

18. Describe briefly the experiments of Boyle, Hooke and Mayow on combustion, and state their conclusions. Give an account of the theory of phlogiston.

[Queen's Univ. Belfast Matric.]

19. Compare and contrast present-day views with those held in the eighteenth century regarding the nature of combustion.

[School Leaving Certificate (Higher), Scotland.]



20. Give as full an account as you can of the discovery of (a) oxygen, (b) the composition of water. [Madras S.L.]

21. Describe the experiments by which it could be proved that air and water contain a common constituent. What is the evidence that in one case this constituent is chemically combined, while in the other it merely forms part of a mixture? [India U.P.]

22. How would you show experimentally that two volumes of hydrogen react with one volume of oxygen to yield two volumes of steam? [Camb. Local Jun.]

23. What is meant by the *partial pressure* of a gas? How can the partial pressure of oxygen in the atmosphere be determined experimentally? [Camb. School Cert.]

24. In an experiment with Victor Meyer's vapour density apparatus, 0.15 gram of a liquid was volatilised. The air displaced and collected in the tube was found to be 26 c.c., the water inside standing 27 cm. above the level of the water in the trough. The atmospheric pressure was 755 mm. and the temperature  $26^{\circ}\text{C}$ . Calculate the vapour density of the substance. Tension of aqueous vapour at  $26^{\circ}\text{C} = 25$  mm. Specific gravity of mercury = 13.5. [Allahabad Inter.]

25. Explain how the volume of a gas in the dry condition can be calculated from observations made of the temperature, pressure, and volume when the gas is collected over water, and the maximum pressure of water vapour at the particular temperature is known. 110 c.c. of hydrogen were collected over water at  $18^{\circ}\text{C}$ . and 740 mm. pressure. Calculate the volume of the gas at normal temperature and pressure, (a) taking account of the pressure of water vapour (15.4 mm. at  $18^{\circ}\text{C}$ .), (b) neglecting the effect of the water vapour. [Camb. School Cert.]

26. What is meant by the diffusion of gases? Describe an experimental method of roughly ascertaining the relative rates of diffusion of two gases, say hydrogen and oxygen. The relative rate of diffusion of a gas as compared with carbon dioxide is as 27 is to 29. Calculate the molecular weight of the gas. ( $\text{C} = 12$ ,  $\text{O} = 16$ .) [London Matric.]

27. State Graham's Law of Diffusion of gases, and describe any experiments you have witnessed relating to diffusion of gases. In 50 seconds 300 c.c. of oxygen diffuse through a porous plate. How long will it take 500 c.c. of chlorine to diffuse through the same plate? Take the molecular weights of oxygen and chlorine as 32 and 72 respectively. [London Gen. School.]

28. Define dissociation. Using a porcelain Victor Meyer apparatus, the following data were obtained for iodine: 0.0874 gm. of iodine displaced 13.7 c.c. of air; barometer, 722.8 mm.; temperature of the room,  $21.5^{\circ}\text{C}$ .; vapour pressure of water at  $21.5^{\circ}\text{C}$ ., 19.2 mm.

Calculate the vapour density of iodine, and the degree of dissociation at the temperature of the experiment. (I, 127.) [Queen's Univ. Belfast Matric.]

29. Describe *two* cases of abnormal vapour density with which you are conversant. How is this abnormality usually explained? Adduce experimental evidence in support of your explanation.

[Central Welsh Board, Higher.]

30. Write an account of the kinetic theory relating to gases.

[Queen's Univ. Belfast Matric.]

31. A piece of camphor left exposed to air loses in weight. Pieces of iron become rusty on exposure in the air and increase in weight. How would you reconcile the above facts with the statement that matter is indestructible?

[Calcutta Inter.]

32. A compound containing sodium, sulphur, oxygen and hydrogen gave on analysis the following result: Na = 14.31 per cent.; S = 9.97 per cent.; H = 6.25 per cent.; O = 69.47 per cent. Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallisation.

[Calcutta Inter.]

33. A solution was known to contain both nitric and hydrochloric acids. For complete neutralisation it was found that 50 c.c. of the acid solution required 42 c.c. of caustic soda solution containing 25 grams per litre, whilst on precipitation with silver nitrate 50 c.c. yielded 2.45 grams of silver chloride. Calculate the weights of hydrochloric and nitric acids, respectively, contained in 1 litre of solution. (Ag = 108, Cl = 35.5, Na = 23, O = 16, N = 14, H = 1.)

[London Matric.]

34. Show that the three results given below illustrate a law of chemical action. Enunciate the law.

(a) 0.46 gm. of magnesium produce 0.77 gm. of magnesium oxide.

(b) 0.82 gm. of magnesium liberate 760 c.c. of hydrogen at N.T.P. from an acid.

(c) 1.26 gm. of water result from the union of 1.11 gm. of oxygen with hydrogen.

[Civil Service, Northern Ireland.]

35. Exactly 3 gm. of magnesite ( $\text{MgCO}_3$ ) were added to 5.000 gm. of dilute sulphuric acid. After all action had ceased, it was found that 0.480 gm. was left undissolved. Calculate the percentage strength of the sulphuric acid. In this reaction what volume of  $\text{CO}_2$  would be evolved measured at  $0^\circ \text{C}$ . and 760 mm. pressure? (Mg = 24.3.)

[Punjab Univ.]

36. Three oxides of lead have the following compositions:

	I	II	III
Lead -	92.85	90.63	86.51 per cent.
Oxygen -	7.15	9.37	13.49 " "

By reference to these compositions illustrate the law of multiple proportions and assign formulae to these three oxides. Pb = 207, O = 16.

[Madras Inter.]



37. State the Law of Constant Composition of chemical compounds and explain how it may be verified for (a) sodium chloride, (b) copper oxide.

38. Describe fully any determinations which you have made on which a law of multiple proportions can be based. In an experiment it was found that 1 gm. of a chloride of iron gave by precipitation with silver nitrate 2.26 gm. of silver chloride, while 1 gm. of another chloride of iron gave by the same method 2.65 gm. of silver chloride. Assuming the composition of silver chloride, show how these results illustrate the law of multiple proportions. ( $\text{Ag} = 108$ ,  $\text{Cl} = 35.5$ ) [Madras Inter.]

39. Two oxides *a* and *b* of a certain metal were heated to constant weight in a current of pure hydrogen, and the water obtained in each case was weighed. The following results were obtained :

2.00 gm. of *a* gave 0.2517 gm. water,  
1.00 gm. of *b* gave 0.2264 gm. water.

Show that the above results illustrate the law of multiple proportions and calculate the equivalents of the metal. [Oxford and Camb. School Cert.]

40. State the law of multiple proportions. A metal forms three oxides which contain 76.47, 68.42 and 52.0 per cent. of metal respectively. Show that these compounds are in agreement with the law of multiple proportions. [Camb. Local Sen.]

41. 3.120 gm. of washing soda (sodium carbonate) crystals were dissolved in 200 c.c. of water. 20 c.c. of the resulting solution titrated with decinormal sulphuric acid solution required 21.80 c.c. for exact neutralisation. Calculate the percentage weight of anhydrous sodium carbonate in the crystals. [Central Welsh Board, Elementary.]

42. Indicate how you would propose to ascertain whether a given solid compound is an acid, a base, or a salt. Discuss the possibility of one and the same body belonging to more than one of the classes. [Camb. Local Sen.]

43. What are the characteristic properties of acids, bases and salts? Give examples of each. What volume of a ten per cent. solution of sodium carbonate will be required to neutralise a litre of a solution containing 4.9 gms. of sulphuric acid? [Calcutta Inter.]

44. Explain what is meant by a base, illustrating your answer by considering the properties and reactions of the hydroxides of sodium, ammonium and zinc.

45. Explain carefully what you mean by an acid salt. Give examples, and describe the preparation of an acid salt from sulphuric acid.

46. Define the terms : 'acid,' 'base,' 'salt,' 'dilute solution,' 'saturated solution,' 'gram-molecule,' 'catalysis,' and 'distillation?' [Queen's Univ. Belfast Matric.]

47. Define the terms 'acid,' 'base,' and 'salt.' What are the different classes of salts? In what different ways can salts, in general, be obtained? Give illustrative examples. [Punjab Univ.]

48. What is meant by a *normal* solution? Concentrated hydrochloric acid has a specific gravity 1.16 and contains 32 per cent. of hydrogen chloride. Calculate the volume of this liquid which would be required to make ten litres of a normal solution of the acid. [Camb. School Cert.]

49. Ten gm. of iron wire were placed in 150 c. of hydrochloric acid containing 30 gm. of hydrogen chloride: calculate (a) the volume of hydrogen evolved, measured at 19° C. and 750 mms. pressure, and (b) the weight of acid left at the end of the reaction. [Joint Matric. Board.]

50. 100 gm. of zinc was placed in 1 litre of dilute sulphuric acid. After all action had ceased the excess of zinc remaining weighed 35 gm. Find the number of grams of sulphuric acid present in the litre of solution. State also what volume of hydrogen (measured at N.T.P.) was evolved. (11.2 litres of hydrogen at N.T.P. weigh 1 gm. O=16, S=32, Zn=65.) [London Gen. School.]

51. From the following table plot the relationship between the densities of solutions of sodium hydroxide and the percentage of the base:

% sodium hydroxide	5	10	15	20	25	30	35	40	45		
Density	-	-	1.06	1.11	1.17	1.22	1.28	1.33	1.38	1.43	1.48

What volume of decinormal sulphuric acid would be neutralised by 25 c.c. of sodium hydroxide solution of density 1.30? (Na=23, O=16.) [Oxford and Camb. School Cert.]

52. A piece of marble weighing 1.05 gm. was placed in 25 c.c. of a given solution of hydrochloric acid. After the action had ceased, it was found that 0.55 gm. of the marble remained unattacked. Calculate the weight of hydrogen chloride (HCl) present in a litre of the acid. Find also the volume of the carbon dioxide produced assuming it to be measured at 17° C. and 750 mm. pressure. (H=1, Cl=35.5, O=16, C=12, Ca=40.) [London Gen. School.]

53. A paraffin candle (C 82%, H 18%) weighs 100 gm. Find the weight of the products formed by the complete combustion of the candle. [Queen's Univ. Belfast Matric.]

54. What do you mean by the term 'equivalent weight'? In an experiment 0.3 gm. of metal was found to liberate 85 c.c. of hydrogen at 0° C. and 760 mm. Find the equivalent of the metal. [Madras S.L.]

55. Five c.c. of sulphuric acid are dissolved in water and the volume made up to 500 c.c.: 10.2 c.c. of this diluted acid neutralised exactly 22.7 c.c. of decinormal sodium carbonate solution. What volume of water must be added to 400 c.c. of the diluted acid in order to make it exactly decinormal? [Calcutta Inter.]



56. The gases obtained by dissolving 0.100 gm. of a metal in dilute acid, and by heating 0.075 gm. of  $\text{KClO}_3$  were mixed in a eudiometer and exploded. The residual hydrogen measured dry at  $27^\circ$  and 680 mm. was 18.10 c.c. Calculate the equivalent of the metal. [Madras Inter.]

57. From the following table plot the relationship between the specific gravities of solutions of hydrochloric acid and the concentration of the acid.

Gm. HCl per litre	469	404	303	273	152	96	12
Specific gravity -	1.2	1.175	1.135	1.125	1.070	1.045	1.005

What volume of decinormal sodium hydroxide would be neutralised by 20 c.c. of hydrochloric acid of specific gravity 1.15? [Camb. School Cert.]

58. State and explain the law of multiple proportions. A certain metal forms two oxides. When 0.5 gm. of the first oxide was heated in a stream of hydrogen 0.1687 gm. of water was obtained, while 0.4 gm. of the second oxide under similar conditions yielded 0.1000 gm. of water. Calculate the equivalents of the metal. [Camb. School Cert.]

59. Describe as fully as you can an experiment to determine the equivalent weight of copper. What further knowledge would you require in order to find its atomic weight? [Central Welsh Board, Elementary.]

60. Illustrate the law of equivalents from the following analyses:

Potassium chloride : potassium 52.5% ; chlorine 47.5%.

Potassium iodide : potassium 23.6% ; iodine 76.4%.

Chloride of iodine : iodine 78.2% ; chlorine 21.8%.

(K 39.1 ; Cl 35.46 ; I 126.9.)

[Queen's Univ. Belfast Matric.]

61. State the principle of two methods of determining the equivalent weight of *either* zinc *or* chlorine, and describe how you would carry out one method in practice.

62. The *equivalent* of oxygen is 7.94. Explain the meaning of this statement. Describe, in full detail, an experiment by which this value has been obtained, emphasising the points of importance necessary to obtain an accurate result. [London Gen. School.]

63. The oxide of a certain metal was found, on analysis, to contain 12.5 per cent. of oxygen. Calculate the equivalent of the metal. What further facts and reasoning are required to fix the atomic weight of the metal? [Camb. Local Sen.]

64. From the following table plot the relationship between the densities of solutions of hydrochloric acid and the percentage of the acid :

% hydrochloric acid -	10.0	12.4	20.3	25.2	31.3	37.2
Density -	1.05	1.06	1.10	1.13	1.16	1.19

What volume of normal sodium hydroxide solution would be neutralised by 25 c.c. of hydrochloric acid of density 1.12? (Cl = 35.5.) [Oxford and Camb. School Cert.]

65. 4.215 gm. of a metallic carbonate were heated in a hard glass tube and the carbon dioxide which was evolved was collected over mercury. It was found to measure 1336 c.c. at 700 mm. and  $27^{\circ}\text{C}$ . What was the equivalent weight of the metal? The molecular weight of a gas at N.T.P. occupies 22.4 litres. [Madras Inter.]

66. 1 gm. of magnesium displaces from combination 0.083 gm. of hydrogen, 9 gm. of silver, and 5.25 gm. of copper. What are the equivalents of these elements? [Madras S.L.]

67. Distinguish between the chemical equivalent and the atomic weight of an element, illustrating your answer by reference to any suitable metallic element. In an experiment, 0.49 gm. of a metal was dissolved in hydrochloric acid, and was found to displace 295 c.c. of dry hydrogen at a temperature of  $22^{\circ}\text{C}$ . and a pressure of 752 mm. of mercury. The specific heat of the metal was found to be 0.152. Calculate the chemical equivalent and the atomic weight of the metal. [School Leaving Certificate (Higher), Scotland.]

68. Write a short account of *either* the evidence for the atomic theory *or* the experiments which led Lavoisier to the modern view of combustion. [Oxford and Camb. School Cert.]

69. Write an account of the history of the atomic theory. [Queen's Univ. Belfast, Entrance Schol.]

70. Explain the connection between the equivalent weight and the atomic weight of an element. It was found that when 0.15 gm. of a metal was treated with dilute acid it yielded 51.3 c.c. of hydrogen at  $0^{\circ}\text{C}$  and 760 mm. Calculate the equivalent weight of the metal. [Camb. School Cert.]

71. Define 'atomic weight' and 'equivalent weight' of an element, and state how these are related to one another. Being provided with metallic lead, give an outline of the method you would follow in order to determine its equivalent weight. [Joint Matric Board.]

72. What do you understand by the atomic weight of an element? Show how it is related to the equivalent weight. By what methods may the atomic weight be found from the equivalent?

73. 0.5 gm. of a metal, M, on solution in dilute hydrochloric acid displaced 637 c.c. of hydrogen, measured at  $16^{\circ}\text{C}$ . and 780 mm. pressure. Calculate the equivalent weight of the metal. If the formula of the oxide of the metal is  $\text{M}_2\text{O}_3$ , what will be the atomic weight of the metal? Write down formulae for the hydroxide, chloride and sulphate of the metal. (1 litre of hydrogen at N.T.P. weighs 0.09 gm.) [Central Welsh Board, Elementary.]

74. Explain carefully, illustrating your answer as far as possible with examples, the various considerations which are taken into account in fixing the atomic weight of an element whose chemical equivalent is known. [Central Welsh Board, Higher.]



75. A volume of 33.6 c.c. of phosphorus vapour weighs 0.0625 gm. at  $546^{\circ}\text{C}$ . and 76 cm. pressure. What is the molecular weight of phosphorus?

76. What is meant by the terms *vapour density*, *molecular weight*? Describe a method for finding the molecular weight of a gas such as nitrogen. [Oxford and Camb. School Cert.]

77. The chloride of a certain metal contains 54.42 per cent. of chlorine. The vapour density of the chloride is 8.16 (oxygen = 1). Calculate the equivalent of the metal and the molecular weight of the chloride. What other information would you require, and how would you use it in order to calculate the atomic weight of the metal? [Madras Inter.]

78. State carefully how the volume of any given mass of gas changes when an increase is made (a) in its temperature without altering the pressure, (b) in its pressure when the temperature remains the same. Describe how you could verify experimentally either (a) or (b). What simple relationship exists between the volumes in which gases combine? Give two examples. State the hypothesis which accounts for this relationship. [Joint Matric. Board.]

79. What is the vapour density of a substance, and of what importance is it in determining chemical formulae? State the reasons that have led to fixing the molecular weight of hydrogen as 2.

80. State clearly the reasoning which has led to the conclusion that the molecule of chlorine consists of two atoms. [London Matric.]

81. On dissolving 0.1 gm. of a metal in hydrochloric acid, 124.3 c.c. of hydrogen at  $15^{\circ}\text{C}$ . and 720 mm. was evolved. Calculate the equivalent of the metal. The chloride of the metal was found to possess a vapour density of 66.6 ( $\text{H} = 1$ ) and contained 79.8 per cent. of chlorine. Calculate the atomic weight and valency of the metal. [London Matric.]

82. The oxide of an element contains 53.0 per cent. of the element and the vapour density of the chloride of the element is 66. Calculate (a) the atomic weight, (b) the valency of the element. Point out clearly what assumptions are made in the course of the calculations. [London Matric.]

83. Enunciate Avogadro's Law and explain its importance in determining the atomic weights of the elements, illustrating your answer by examples. [Calcutta Inter.]

84. What is Avogadro's hypothesis? Explain, with illustrations, how this hypothesis brings into harmony Dalton's atomic theory and Gay-Lussac's law of combining volumes. [Dacca Inter.]

85. State (a) Gay-Lussac's law of volumes and (b) Avogadro's hypothesis. Calculate the composition by volume of a mixture of carbon monoxide and methane, 10.5 c.c. of which required 9 c.c. of oxygen for complete combustion. [Camb. School Cert.]

86. State the law of atomic heats as defined by Dulong and Petit. 0.91 gm. of the sulphide of a metal when roasted in air produced 263.5 c.c. of sulphur dioxide at  $27^{\circ}$  and 710 mm. pressure. The specific heat of the metal was found to be 0.0533. Ascertain the atomic weight of the metal. [Bombay Inter.]

87. Define (a) atomic weight, (b) molecular weight. One gm. of a metal, when acted upon by a solution of sodium hydroxide liberated 1242 c.c. of hydrogen, measured at  $0^{\circ}$  C. and 760 mm. The specific heat of the metal is 0.22. What is its atomic weight? How is the value thus found supported by the fact that the vapour density of the chloride is 4.6 times that of air? [Madras Inter.]

88. What do you understand by a colloidal solution? Describe the preparation of a colloidal solution of a metal. How may a colloid be separated from a crystalloid with which it is in solution? Give an illustrative example. [Central Welsh Board, Higher.]

89. What do you understand by the osmotic pressure of a substance in solution, and how is it determined experimentally? According to Pfeffer, a 4 per cent. solution of sugar showed an osmotic pressure of 2082 mm. of mercury at  $15^{\circ}$  C. Calculate the molecular weight of the sugar. [Central Welsh Board, Higher.]

90. State what is meant by the valency of an element and explain how it may be determined.

91. Discuss the use of the conception of valency to the chemist and show how the valency of an element is related to oxidation and reduction changes. Illustrate your answer as far as possible with examples. [Central Welsh Board, Higher.]

92. What do you understand by *electrolysis*? Describe, in some detail, experiments relating to (a) dilute sulphuric acid, (b) a solution of copper sulphate, in illustration of your answer. Name two important applications of electrolysis. [London Gen. School.]

93. What is meant by electrolysis? Describe the changes which occur when an aqueous solution of (a) copper sulphate, (b) sodium chloride, is electrolysed. [Oxford and Camb. School Cert.]

94. Explain, by describing particular examples, how (a) an electric current, (b) an electric spark, and (c) a silent electric discharge, may be employed to bring about chemical changes. [London Matric.]

95. What is meant by the terms 'reduction' and 'oxidation'? Illustrate your answer by examples. What tests would you apply to a given substance to show whether it is a reducing agent or an oxidising agent? [Camb. School Cert.]

96. Hydrogen sulphide and carbon monoxide are frequently described as *reducing agents* while chlorine and nitric acid are termed *oxidising agents*. Explain the meaning of these terms and describe experiments with these substances which illustrate this classification. [Camb. School Cert.]



**97.** 'Chlorine, which does not contain oxygen, is an oxidising agent.' Explain this statement. What experiments would you make in order to prove it? [Madras Inter.]

**98.** Explain the meaning of the terms 'oxidation' and 'reduction' by describing typical experiments involving these processes which you have carried out in the laboratory.

[Central Welsh Board, Elementary.]

**99.** Explain what you understand by the following terms, illustrating your answer by one example in each case: (a) the valency of an element, (b) acid salts, (c) reversible reactions, and (d) catalysis.

[Joint Matric. Board.]

**100.** Explain briefly the terms catalysis, acid salt, double decomposition, and allotropic modification. Give two examples to illustrate each of these terms.

[Joint Matric. Board.]

**101.** Explain the terms: 'oxidising agent' and 'reducing agent.' Select from the following substances two examples of each, and write an account of the experiments you would perform with them to illustrate your answer: hydrogen, carbon monoxide, chlorine, sulphur dioxide, nitric acid, potassium permanganate.

[School Leaving Certificate (Higher), Scotland.]

**102.** An electric current was passed successively through voltameter cells containing (1) dilute sulphuric acid, (2) copper sulphate (using copper electrodes), (3) silver nitrate (using a silver anode and a platinum cathode). The hydrogen evolved in the first cell was collected over water, and its volume found to be 72.6 c.c. measured at  $13^{\circ}\text{C}$ . and 765 mm. pressure. The increases in weight of the cathodes in cells (2) and (3) were respectively 0.195 gm. and 0.661 gm. Calculate the chemical equivalents of hydrogen and copper, taking that of silver as 107.9. (Pressure of aqueous vapour at  $13^{\circ}\text{C}$ . = 11 mm. of mercury. One litre of hydrogen at N.T.P. weighs 0.09 gm.)

[Punjab Univ.]

**103.** State, from your own experience, three conditions which may influence the rate of a chemical reaction, and give two examples to illustrate the effect of each.

[Univ. of Lond. Matric.]

**104.** Say fully what you understand by a 'reversible reaction.' Discuss the effect of (a) temperature, (b) pressure, on such a reaction, illustrating your answer by reference to (a) the dissociation of phosphorus pentachloride, (b) the dissociation of hydrogen iodide, (c) the effect of heat on barium peroxide.

[Central Welsh Board, Higher.]

**105.** Define and illustrate the terms (a) reducing agent, (b) electrolysis, (c) oxidation, (d) hydrolysis, (e) double decomposition, (f) reversible reaction.

[Queen's Univ. Belfast, Entrance Schol.]

**106.** What do you understand by 'electrolytic dissociation'? Indicate briefly the grounds on which the theory of electrolytic dissociation was established. How does this theory account for (a) the colour of salt solutions, (b) the heat of neutralisation of acids?

[Central Welsh Board, Higher.]

107. How would you proceed to determine the equivalent weight of copper by an electrolytic method? [Central Welsh Board, Elementary.]

108. Compare and contrast the thermal dissociation of phosphorus pentachloride with the electrolytic dissociation of common salt in aqueous solution. Indicate briefly how the degree of dissociation may be determined in each case. [Central Welsh Board, Higher.]

109. Explain and illustrate by examples the meanings of the following terms: electrolytic dissociation, eutectic mixture, exothermic compound, complex ion, basic salt. [Central Welsh Board, Higher.]

110. Write an account of the periodic classification of the elements. [Queen's Univ. Belfast, Matric.]

111. State the Law of Mass Action and give an example of its application. [Central Welsh Board, Higher.]



## ANSWERS TO QUESTIONS

9.  $24^{\circ}$ ,  $39.0$ ;  $70^{\circ}$ ,  $59.4$ .      24.  $70.86$ .
25. (a)  $98.4$  c.c. (b)  $100.5$  c.c.      26.  $50.8$ .      27.  $125$  sec.
28.  $82.6$ ; Let  $x$  = degree of dissociation, then  $N$  molecules of  $(I_2)$  give  $(1-x)N$  molecules of  $I_2$  and  $2Nx$  molecules of  $I$ ;  $\therefore$  No. of molecules after dissociation  $= (1-x)N + 2xN = (1+x)N$ ;  
 $\therefore \frac{\text{vol. after dissociation}}{\text{vol. before dissociation}} = \frac{1+x}{1}$ ;  
 $\therefore \frac{\text{density after dissociation}}{\text{density before dissociation}} = \frac{1}{1+x} = \frac{82.6}{127}$ ;  
 $\therefore x = 0.538$  or  $53.8$  per cent.
32.  $Na_2SO_4 \cdot 10H_2O$ .      33.  $12.46$  gm.  $HCl$ ;  $11.57$  gm.  $HNO_3$ .
35.  $58.59$ ;  $669.6$  c.c.      36. I.  $PbO$ ; II.  $Pb_3O_4$ ; III.  $PbO_2$ .
41.  $37.02$ .      43.  $53$  c.c.      48.  $983$  c.c.
49. (a)  $4334$  c.c. (b)  $16.96$  gm.      50.  $98$  gm.;  $22.4$  lit.
51.  $2.19$  lit.      52.  $7.3$  gm.;  $120.5$  c.c.
53.  $300$  gm.  $CO_2$ ;  $162$  gm.  $H_2O$ .      54.  $39.2$ .      55.  $490$  c.c.
56.  $19.93$ .      57.  $1850$  c.c.      58.  $18.7$ ; 28.      63.  $56$ .
64.  $180$  c.c.      65.  $12.15$ .
66.  $Mg = 12.05$ ;  $Ag = 108.4$ ;  $Cu = 63.3$ .      67.  $20.15$ ;  $40.3$ .
70.  $32.75$ .      72.  $9.079$ .      73.  $27.24$ .      75.  $125$ .
77.  $29.6$ ;  $261.12$ .      81. equiv.  $10.04$ ; valency  $3$ .
82. at. wt.  $27.09$ ; valency  $3$ .      85.  $8.0$  c.c.  $CO$ ;  $2.5$  c.c.  $CH_4$ .
86.  $116.5$ .      87.  $27.04$ .      89.  $345$ .      102.  $1.01$ ;  $31.83$ .





*PART II*

SOME NON-METALLIC ELEMENTS AND THEIR  
IMPORTANT COMPOUNDS





## CHAPTER XVI

### OXYGEN AND OZONE

**The non-metallic elements.**—The chemical elements are, for convenience, divided into two large groups: the **metals** and the **non-metals**. The line of distinction is not always very sharp, and we shall leave the discussion of the principal differences between the two classes of elements until we come to deal with the metals. The **non-metallic elements** to be described are: **oxygen**, **hydrogen**, **chlorine**, **bromine**, **iodine**, **sulphur**, **nitrogen**, **phosphorus**, and **carbon** and their more important compounds, although a few others, such as **boron**, are briefly mentioned.

The description of the chemistry of a substance includes certain common topics, and the choice of the following will be convenient: **history**, **occurrence**, **preparation** (including industrial preparation, when this is of interest), **properties**, **uses**.

The properties will include:

Physical:	Chemical:
<i>state</i> (solid, liquid, gas);	whether <i>combustible</i> or a
<i>colour</i> ;	<i>supporter of combustion</i> ;
<i>smell</i> ;	<i>acidity</i> or <i>alkalinity</i> ;
<i>taste</i> ;	<i>reactions</i> with other sub-
<i>ease of liquefaction</i> (if a gas);	<i>stances</i> .
<i>density</i> .	

Methods commonly used for the **preparation** of a substance in the laboratory should be distinguished from those methods of **formation** of theoretical interest only, and from **technical processes**.

### OXYGEN

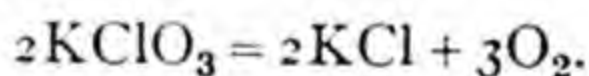
**History.**—Oxygen was discovered by Scheele about 1772 (see p. 98), and independently by Priestley in 1774, by heating

red oxide of mercury (p. 99). Its importance in combustion and respiration was first clearly recognised by Lavoisier (p. 101).

**Occurrence.**—Oxygen occurs as a gas free in the *atmosphere* to the extent of 23 per cent. by weight or 21 per cent. by volume. It occurs in combination in *water*, in nearly all *rocks*, in *plants*, and in *animals*. Oxygen forms about 50 per cent. of the weight of the crust of the earth, and is the most abundant element there.

Oxygen gas is of great importance in *respiration* (p. 424). The breathing of air deficient in oxygen is dangerous, so that in confined spaces, and at high altitudes (where the air pressure is low), oxygen must be supplied. Oxygen gas (*not* liquid) is sold compressed in black steel cylinders under 120 atmospheres pressure and is applied to a variety of purposes, particularly for blowpipes used in cutting and welding metal, and in medicine in cases of pneumonia. These cylinders should be kept cool and not exposed to mechanical shocks. Special reducing valves are used to obtain a steady stream of gas.

**Preparation of oxygen.**—In the laboratory, oxygen is usually prepared by the action of heat on the salt **potassium chlorate**,  $\text{KClO}_3$ . When the crystals of this salt, which are anhydrous (*i.e.*, free from water of crystallisation), are heated fairly strongly in a hard glass tube, they crackle (or *decrepitate*), and then fuse. At a temperature a little higher than the melting point, the salt decomposes slowly, with evolution of oxygen gas in small bubbles, and potassium chloride,  $\text{KCl}$ , a difficultly fusible solid, remains in the tube :



Partly owing to complications in the decomposition (p. 328) and partly owing to the high temperature required (so that an ordinary glass tube or flask is softened and often perforated), the decomposition of potassium chlorate alone is hardly ever used in the laboratory for the preparation of oxygen. A mixture called 'oxygen mixture', consisting of coarsely powdered chlorate with manganese dioxide, evolves oxygen *rapidly* at a much lower temperature than chlorate alone, without fusion, and the chlorate passes directly to the chloride. (Explosions occur if the manganese dioxide contains powdered coal or antimony sulphide and a *little* oxygen mixture should first be tested by heating in an open test-tube.) The mixture is heated in a large test-tube clamped in a horizontal position, and fitted with a fairly wide glass delivery tube passing through a cork in the test-tube and dipping at the other end beneath the water in a pneumatic



trough. Over this end is supported a glass cylinder full of water and standing on a beehive shelf in the trough (Fig. 180). The mixture is cautiously heated, beginning at the end near the cork, and the flame withdrawn from time to time when the evolution of gas begins to be violent. When the air is displaced from the tube, the cylinder is placed on the shelf and the gas collected. The jar when full is closed with a greased ground glass plate

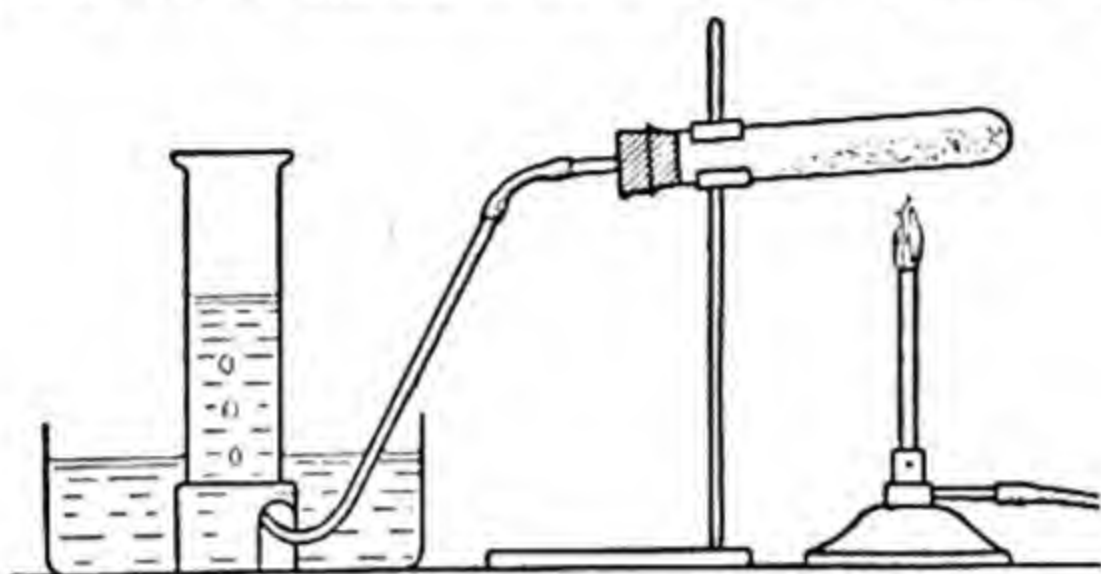


FIG. 180.—THE PREPARATION OF OXYGEN GAS BY HEATING A MIXTURE OF POTASSIUM CHLORATE AND MANGANESE DIOXIDE.

fitting over a ground rim on the cylinder, and is lifted from the trough. The delivery tube must be taken out of the water before the test-tube is allowed to cool, since otherwise water will be forced back into the hot tube and crack it.

**Catalysis.**—The manganese dioxide in the preparation of oxygen undergoes no *permanent chemical* change: it may be recovered from the residue by washing out the potassium chloride with water.

This action of manganese dioxide, discovered by Döbereiner in 1820, is an example of numerous reactions in which *a substance accelerates a chemical reaction without itself undergoing any permanent chemical change*.

Such substances were called **catalysts** by Berzelius (1835) and their action **catalytic action**, or **catalysis** (sometimes **contact action**). Many examples of catalysis will be met with in the further study of the chemical elements (see Index under 'catalysis').

A catalyst may take part in the reaction, but if it does it must be set free again and so remain as such in the final products. It may also undergo physical change: the manganese dioxide left in the oxygen reaction is more finely divided.

**Industrial preparation of oxygen.**—On the technical scale oxygen is nearly always obtained from air. It may be separated from the nitrogen by chemical or physical means. Formerly

chemical methods were used (p. 222), but all the oxygen now used is obtained by a physical process depending on the

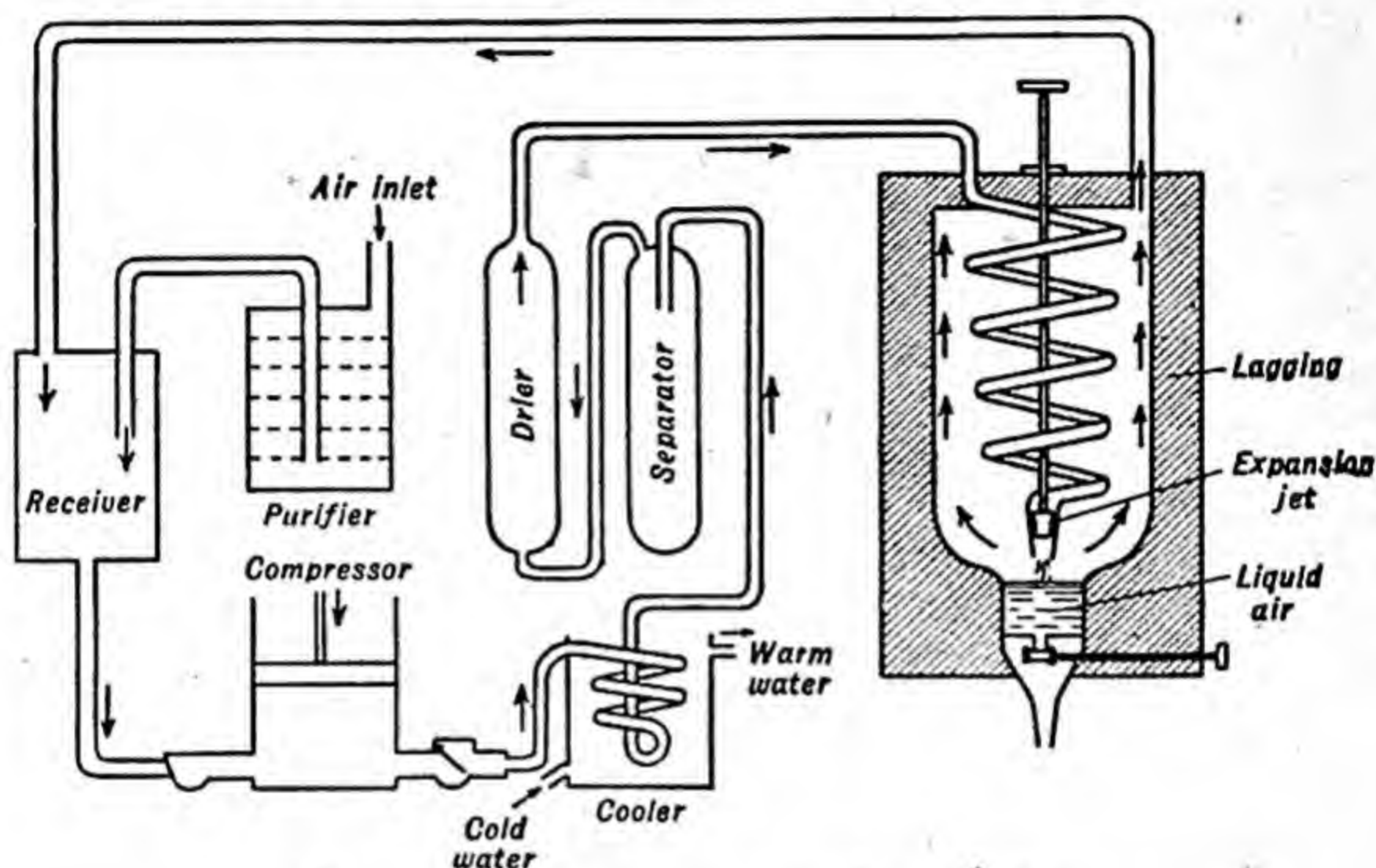


FIG. 181.—PRODUCTION OF LIQUID AIR.

THE AIR IS DRAWN BY A PUMP THROUGH A PURIFIER, AND IS COMPRESSED. THE HEAT PRODUCED BY COMPRESSION IS TAKEN OUT BY A COOLER, AND THE AIR THEN PASSES THROUGH APPARATUS IN WHICH MOISTURE IS REMOVED. THE COMPRESSED AIR EXPANDS THROUGH A JET, AND BECOMES COOLED. THE COLD AIR SWEEPS OVER THE PIPE BRINGING THE COMPRESSED AIR TO THE JET AND COOLS IT BEFORE EXPANSION. THE AIR FINALLY BECOMES SO COLD THAT IT LIQUEFIES.

*liquefaction and fractional distillation of air.* Nitrogen boils at a lower temperature ( $-196^{\circ}$ ) than oxygen ( $-183^{\circ}$ ), and boils off first from liquid air.

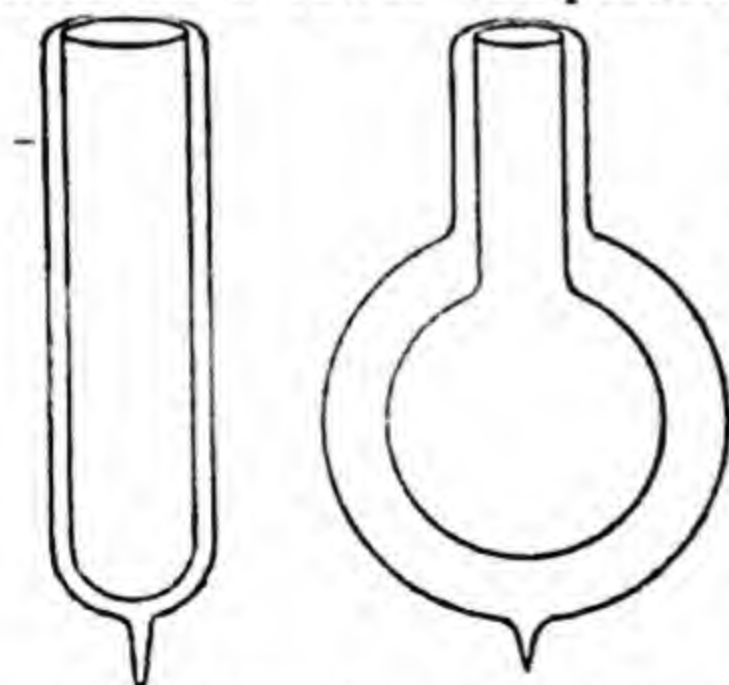


FIG. 182.—DOUBLE-WALLED VACUUM VESSELS FOR HOLDING LIQUID AIR.

The process of liquefying air is shown diagrammatically in Fig. 181. In expanding through a jet the air molecules are separated against slight attractive forces between them, and the energy for this *internal work* is taken from the heat of the gas, which becomes colder. The cooling effect is made cumulative, as shown. Liquid air rapidly evaporates unless kept in a *Dewar vessel* ('thermos flask')



(Fig. 182), consisting of a double-walled bottle with a vacuum between the walls, which are silvered in the annular space. This checks the passage of heat by conduction and radiation. Larger quantities of liquid air or liquid oxygen are

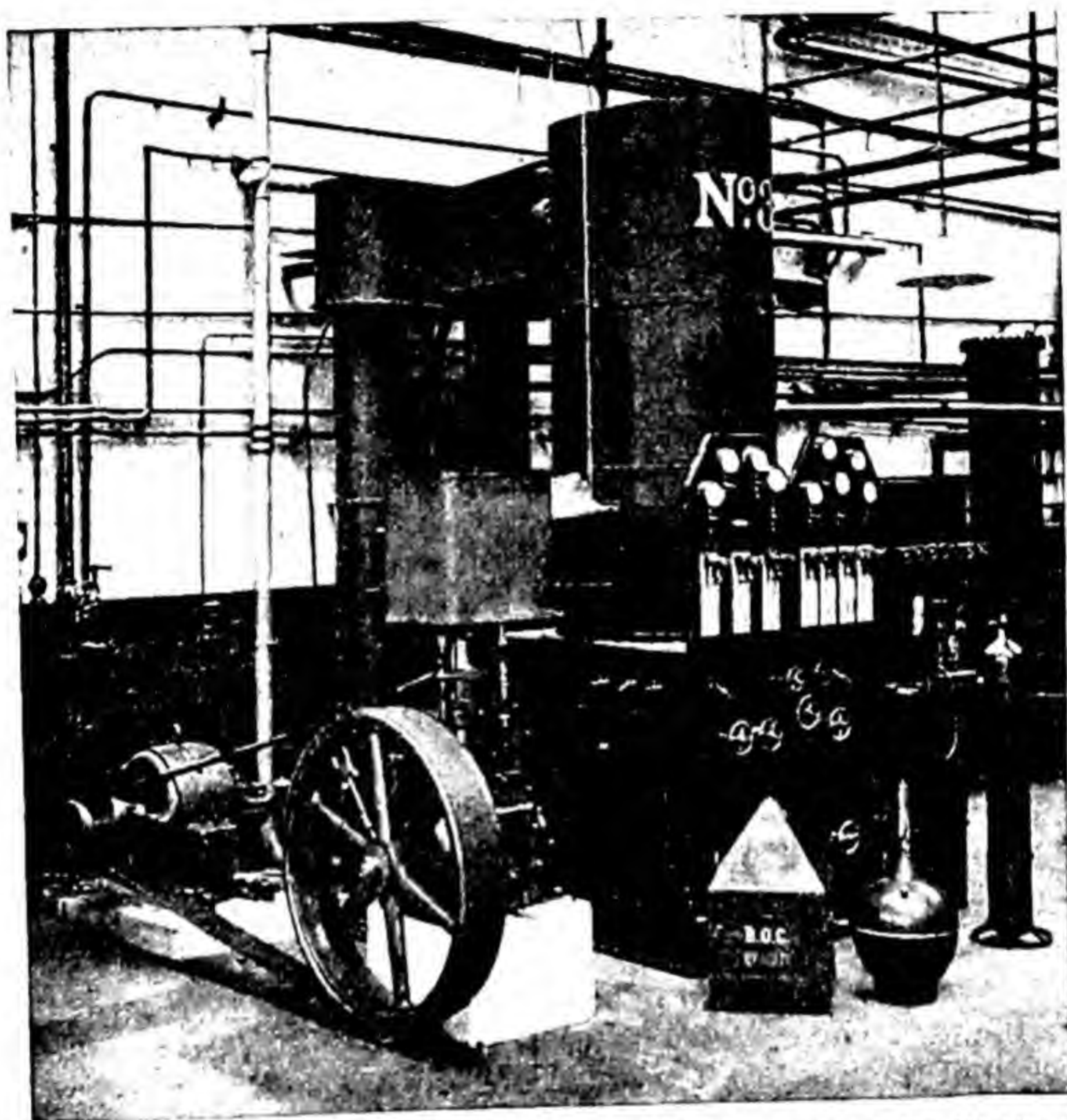


FIG. 183. CLAUDE OXYGEN PLANT PRODUCING 125 CUBIC METRES OF OXYGEN PER HOUR

(By permission of the British Oxygen Co., Ltd.)

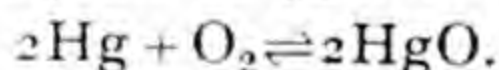
kept in spherical double-walled metal vacuum vessels, shown on the right in Fig. 183.

The liquid air enters the top of a fractionating column (cf. Fig. 323) at  $-194^{\circ}$ , and passes down by way of perforated trays which are covered with liquid, through which the gas bubbles. The nitrogen (b.pt.  $-196^{\circ}$ ) begins to evaporate, and the liquid passing down is enriched in oxygen, its temperature becoming

a little higher, and this liquid collects in a pot below. Here it is heated by compressed air in a coil going to the expansion jet, and evaporates until it is practically pure oxygen at  $-183^{\circ}$ . The oxygen gas rising from this liquid passes through the liquid air coming down the tower, some of it is condensed and evaporates off a portion of nitrogen. Thus the liquid flowing from the base of the tower becomes nearly pure oxygen, whilst the gas passing out of the top is mainly nitrogen.

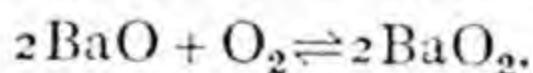
Fig. 183 shows a modern Claude expansion engine plant, operating in the Wembley factory of the British Oxygen Company. The maximum pressure attained during preliminary cooling does not exceed 35 atmospheres, and when oxygen is being produced the working pressure is about 25 atmospheres. These are considerably lower working pressures than can be obtained with the Linde apparatus. The plants are fitted with apparatus to enable a portion of the waste nitrogen to be abstracted in a state of purity, and with further equipment to enable argon to be collected, that rare gas being now of considerable commercial value (p. 398). The cooling of the gas in this type of plant is obtained largely by allowing the gas to expand and do work in an engine, which can be seen on the left of the column, and the heat exchangers at the back.

When mercury is heated in air it abstracts the oxygen from it, forming mercuric oxide,  $\text{HgO}$ , which at a higher temperature decomposes into mercury and oxygen:



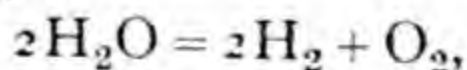
A limited supply of mercury could therefore be used to abstract the oxygen from a large quantity of air, but the method is not suitable for technical use.

Barium monoxide ('baryta'), when heated to dull redness in air, takes up oxygen to form barium peroxide, which when heated to bright redness or exposed to reduced pressure, loses oxygen again:



This reaction was formerly used in the Brin process, which is now entirely obsolete.

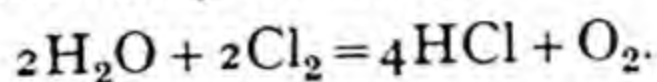
**Oxygen from water.**—Oxygen may be obtained from water by electrolysis (p. 110):



a process which has been used on the technical scale. Oxygen is also formed by passing a mixture of steam and chlorine gas



through a heated silica tube filled with broken porcelain. The chlorine removes the hydrogen from the water to form hydrochloric acid, which may be washed out with water, and sets free the oxygen, which may be collected :



This is not a satisfactory method for preparing oxygen, but is interesting as a chemical means of separating the oxygen from water.

**The properties of oxygen.**—Oxygen is a colourless gas, without smell or taste. It is very slightly heavier than air. Air is a mixture of four volumes of nitrogen (density 14) and one volume of oxygen (density 16) ; its density will be given by the usual formula :  $\frac{4 \times 14 + 16}{5} = \frac{72}{5} = 14.4$ , whilst that of oxygen is 16, or 1.11 times that of air.

Oxygen is slightly soluble in water : the small amount of oxygen dissolved in natural waters is sufficient for the respiration of fish. Oxygen is difficult to liquefy : the liquid is pale blue in colour and is slightly magnetic.

The chemical properties of oxygen are chiefly concerned with combustion, and in this way, as well as in respiration, it enters continually into everyday life.

**Combustion.**—The combination of substances with oxygen, when attended with the evolution of heat and light, is called combustion. Substances which burn in air do so with greatly enhanced brilliancy in pure oxygen, since the nitrogen in air acts as a diluent, absorbing part of the heat given off in the combustion. Many substances, such as phosphorus, oxidise slowly when exposed to air or oxygen, without catching fire, because the heat produced is dissipated too rapidly to raise the mass to the ignition point. Oily cotton-waste, or damp hay, however, may become heated to the ignition point if stored in heaps exposed to air. This slow process of oxidation is known as **autoxidation**. The 'drying' of oil-paint or varnish is really a process of autoxidation. The linseed oil in the paint or varnish slowly absorbs oxygen from the air and becomes solid. The process may be hastened by adding salts of certain metals (*e.g.*, lead and manganese) which act as catalysts and are called 'driers.'

Fine coal containing iron pyrites (iron disulphide,  $\text{FeS}_2$ ) is liable to catch fire spontaneously if left about in mines, producing what are called 'gob-fires' Rotten wood is slowly

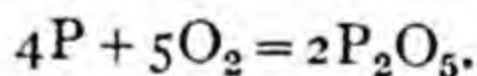
oxidised away by bacterial action, and very often glows in the dark. The fading of coloured fabrics on exposure to light is usually accompanied by oxidation. Sewage is purified by free exposure to air, so that oxygen is dissolved and acts upon the organic matter in presence of bacteria. Vinegar (a weak solution of acetic acid) is made by the oxidation of the alcohol in beer or wine when exposed to air in presence of a ferment.

**Experiments on combustion.**—The combustion of solids, such as phosphorus, sulphur, and carbon in oxygen may be demonstrated by the following experiments. The substances are contained in the bowls of *deflagrating spoons*, ignited by heating in a flame, and placed in jars of oxygen (Fig. 184).

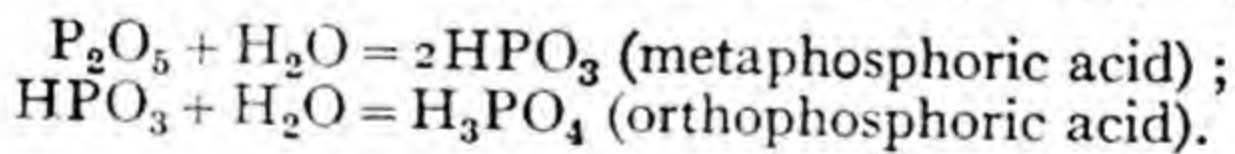


FIG. 184.—GAS JAR AND DEFLAGRATING SPOON.

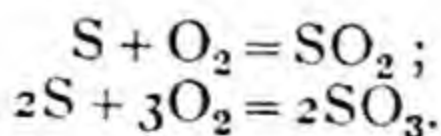
The white phosphorus is cut under water, a small piece rapidly dried by pressing between filter papers, and put in the spoon with dry crucible tongs. *The dry phosphorus must on no account be handled with the fingers*, as it may take fire. The phosphorus burns in oxygen with an exceedingly brilliant white flame, producing a dense white cloud of phosphorus pentoxide which settles in flocks on the sides of the jar if this is quite dry :



When water is poured into the jar the oxide dissolves, and phosphoric acid is formed, which changes the colour of blue litmus to red :

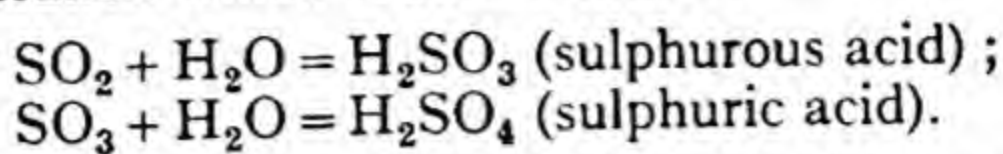


A piece of roll sulphur when ignited in a spoon burns with a bright blue flame when introduced into a jar of oxygen. The gas sulphur dioxide,  $SO_2$ , is the main product of the combustion, but a little solid sulphur trioxide,  $SO_3$ , is also formed, which renders the gas slightly cloudy :

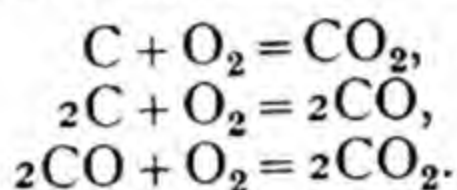




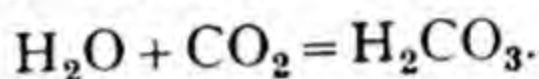
When shaken with water, the products of combustion dissolve, yielding a solution which reddens litmus :



A piece of wood charcoal strongly heated in a spoon burns brightly, often throwing off bright sparks, when placed in oxygen. Carbon dioxide,  $\text{CO}_2$ , is the chief product of the reaction, although a little carbon monoxide,  $\text{CO}$ , is generally formed. A flame seen over the burning charcoal is due to the combustion of the carbon monoxide to carbon dioxide :



When shaken with water, a little carbon dioxide dissolves, forming a solution of the very unstable **carbonic acid**,  $\text{H}_2\text{CO}_3$ , which changes the blue colour of litmus to a port-wine red colour, quite different from the bright red produced by the other acids :



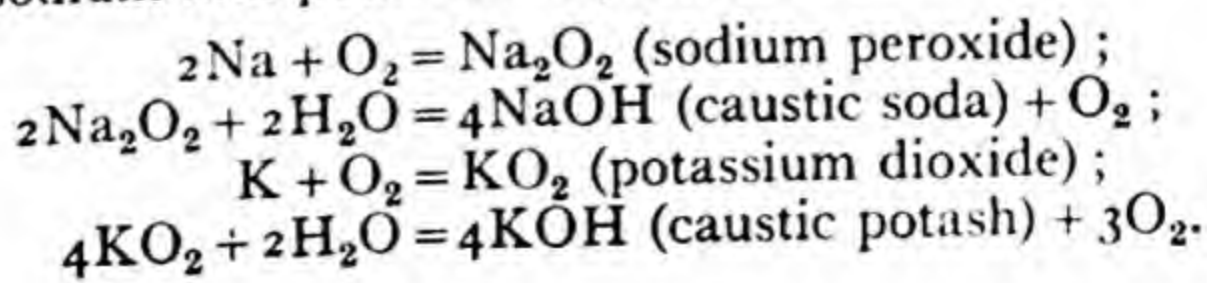
Carbon monoxide is insoluble in water and has no action on litmus.

Phosphorus, sulphur, and carbon on combustion give **acidic oxides**, *i.e.*, oxides which yield acids on solution in water (p. 145).

Some metals burn in oxygen to form **basic oxides**, *i.e.*, oxides reacting with acids to form salts (p. 146).

Magnesium ribbon, if ignited in air and inserted into a jar of oxygen, burns with a blinding white light, forming white solid magnesium oxide,  $\text{MgO}$ , which is a weakly basic oxide, and turns red litmus paper blue when moistened and laid upon it.

Sodium and potassium, when heated in iron deflagrating spoons until they begin to burn, and then lowered into *dry* jars of oxygen, burn with bright yellow and purple flames, respectively, forming orange-yellow solid **peroxides** which, *when cold*, may be dissolved in water with evolution of oxygen and formation of strongly alkaline solutions which turn red litmus blue and contain sodium and potassium hydroxides :



A spiral of iron wire, tipped with a bit of burning wood, burns brilliantly, giving off a shower of bright sparks, when lowered into a bottle of oxygen (Fig. 185). Black oxide of iron,  $\text{Fe}_3\text{O}_4$ , is formed in fused globules, which fall on a layer of sand. Oxide of iron has no action on litmus.

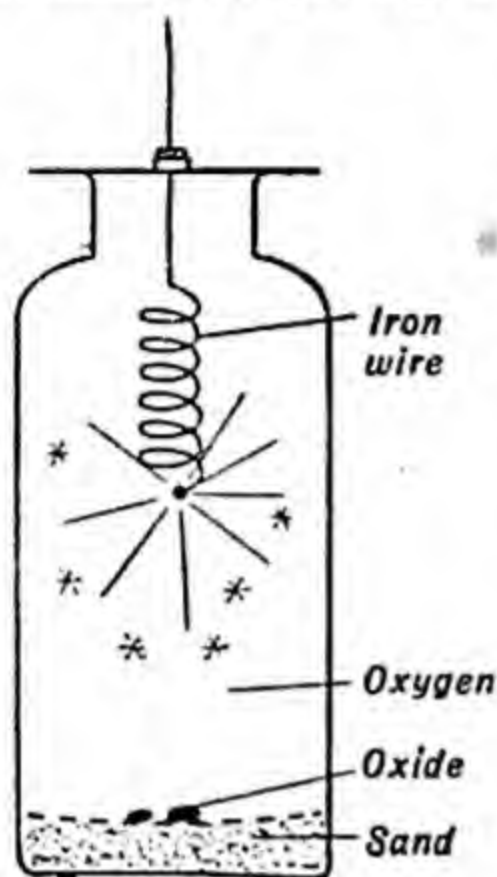


FIG. 185.  
IRON WIRE BURNING IN  
OXYGEN GAS.

A jet of hydrogen burns in a jar of dry oxygen, producing water, which (Fig. 186) condenses in drops on the cold sides of the jar:  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ . If a jet of oxygen is thrust into an inverted jar of hydrogen, burning at the mouth, the oxygen takes fire, and continues to burn in the atmosphere of hydrogen (Fig. 187). The terms combustible, and supporter of combustion, are, therefore, purely relative.

Many combustible substances, in a finely divided condition, ignite spontaneously in air or oxygen. For example, finely divided lead, called pyrophoric lead, catches fire and glows when a tube containing it is cut open and the powder shaken out into the air: fumes of lead oxide are

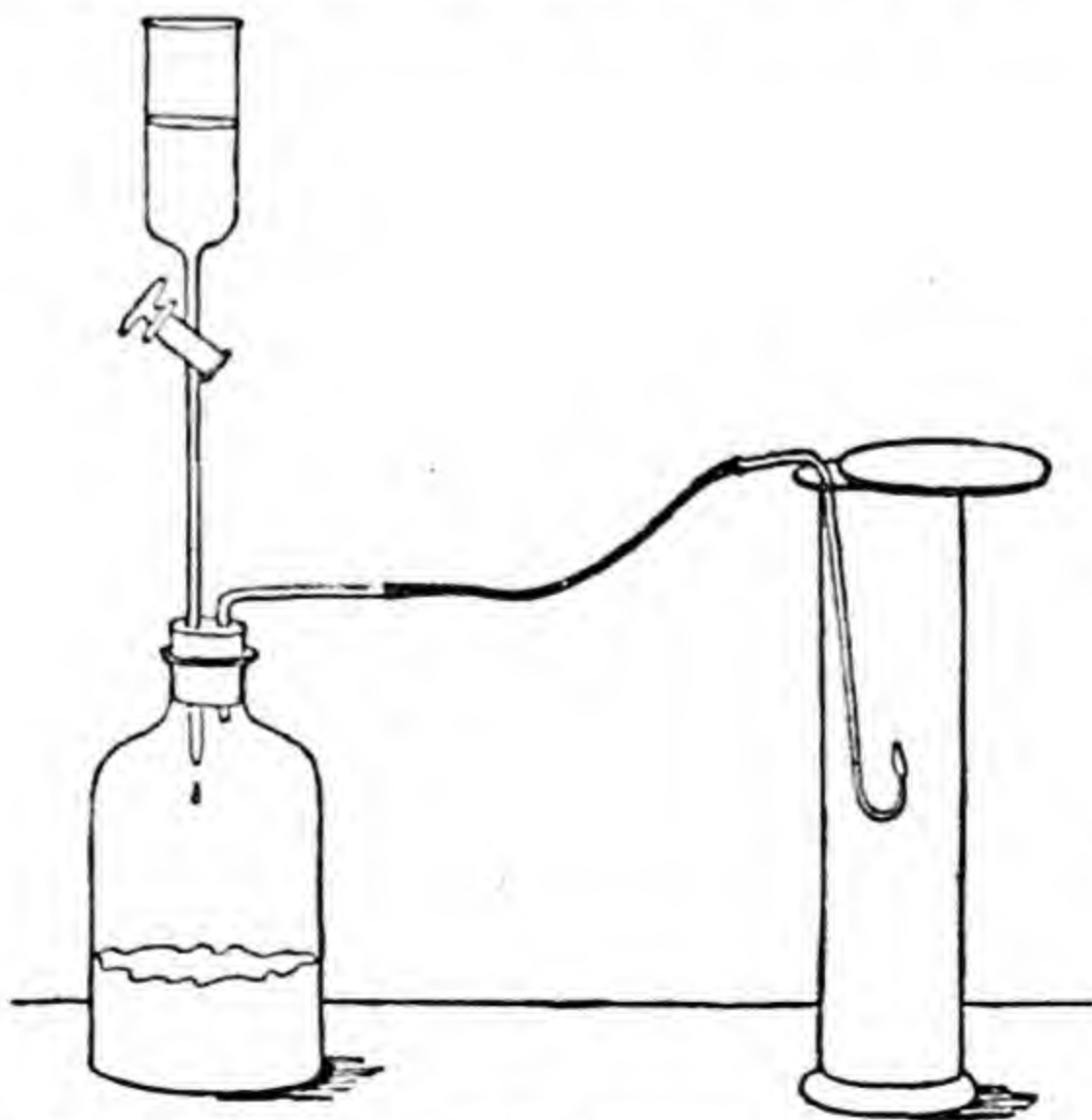


FIG. 186.—HYDROGEN BURNING IN OXYGEN.

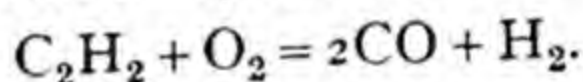


formed. (Pyrophoric lead is made by heating lead tartrate.) Finely divided phosphorus, left when a solution of white phosphorus in carbon disulphide is allowed to evaporate spontaneously on a piece of blotting paper, also ignites spontaneously in air.

**Technical uses of oxygen.**—Compressed oxygen gas is used for the oxy-hydrogen and oxy-acetylene blowpipes.

When oxygen and hydrogen are supplied separately to a blowpipe jet consisting (Fig. 188) of two concentric tubes, the oxygen being inside, a blue, pointed, intensely hot flame is produced, in which platinum wire readily melts. If the oxy-hydrogen (or oxy-coal gas) flame impinges on a small cylinder of quicklime, which is very infusible, an intensely white light (limelight) is emitted by the incandescent lime.

In the oxy-acetylene blowpipe (Fig. 189), acetylene gas takes the place of hydrogen, and the flame is so hot that steam is practically completely dissociated, and the reaction is



The flame is therefore strongly reducing, which makes it very suitable for *welding metals*.



FIG. 188.—THE OXY-HYDROGEN BLOWPIPE (SECTION).  
HYDROGEN ENTERS THROUGH H AND OXYGEN THROUGH O.

In *cutting* iron or steel a third tube is used inside the other two, and when the metal is heated by the flame to a high temperature, this inner oxygen jet is turned on. The iron itself then burns brilliantly, emitting showers of sparks, and rapidly fuses away. Since the oxygen jet is narrow, a very clean cut is produced. Plates of steel can be rapidly cut through.

Coal gas can be used in this blowpipe. Steel ships and the framework of buildings can be cut up rapidly by the blowpipe, which is also used by the scientific burglar in open-

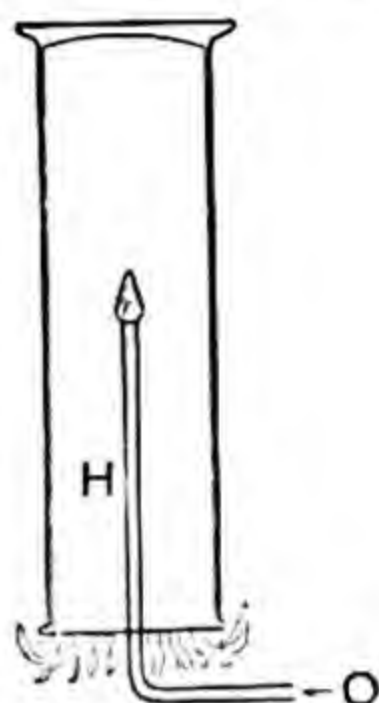


FIG. 187.  
OXYGEN BURNING  
IN HYDROGEN.

ing safes. Gear wheels are hardened under water with the blowpipe.

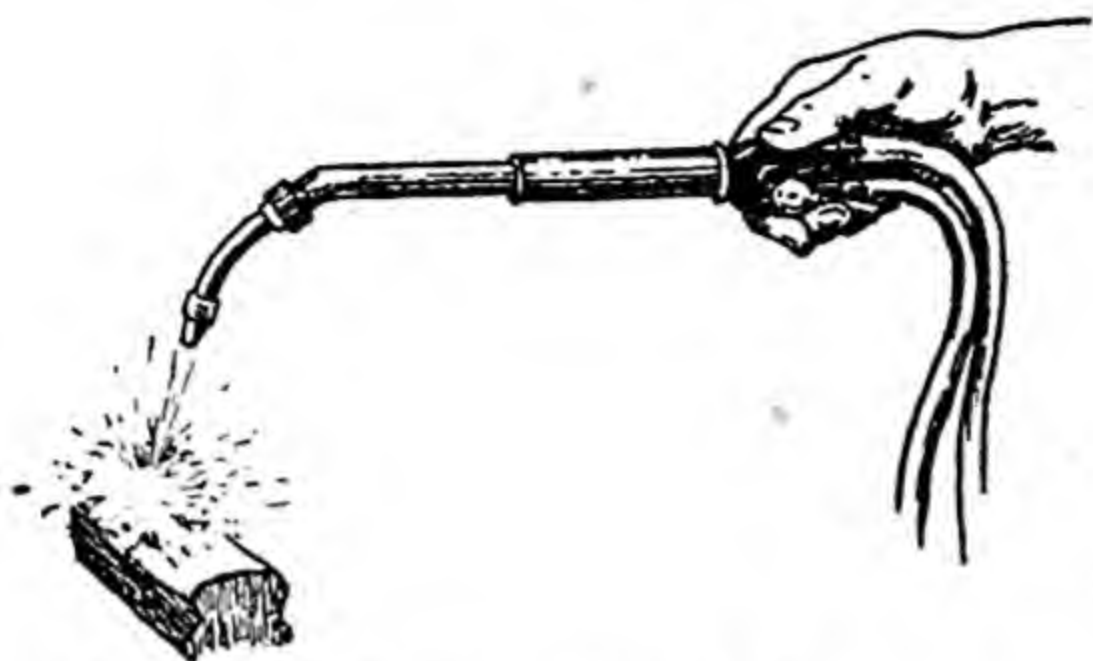


FIG. 189.—OXY-ACETYLENE BLOWPIPE.

Liquid oxygen finds a use in admixture with charcoal powder and oil as an explosive, which is used in the Lorraine iron mines and served in the blasting of the Simplon Tunnel. If the shot does not fire, the liquid oxygen evaporates and it becomes harmless.

Liquid oxygen, kept in large metal Dewar vessels (shown in the lower right-hand corner of Fig. 183), is also used to provide oxygen gas for rescue work in mines. The gas is used mixed with some carbon dioxide, which stimulates respiration. Ether vapour used as an anaesthetic is administered mixed with oxygen.

The *test for oxygen* is the rekindling of a glowing chip: nitrous oxide also gives this result but can be distinguished from oxygen by other tests (p. 395).

**Heat of combustion.**—By the combustion of substances in oxygen large amounts of heat are given out. In everyday life we generally make use of the combustion of coal or gas in air (containing oxygen) as a source of heat. Chemical reactions accompanied by the *evolution of heat* are called **exothermic**.

In the decomposition of mercuric oxide heat must be applied, and the reaction, which is accompanied by the *absorption of heat*, is called **endothermic**.

Coal-gas is now sold on a basis of **calorific value**, *i.e.*, the heating value of the gas when burnt. The unit of calorific value is the **therm**. This is based on a unit of heat different from the calorie, viz. the **British thermal unit (B.Th.U.)**, which



is the amount of heat required to raise the temperature of one *pound* of water through one *degree Fahrenheit* (B.Th.U. = 250 calories). A therm is 100,000 B.Th.U. 500 B.Th.U.'s per cubic foot is a common value for town gas. This is a much fairer method than the old way of simply charging so much per thousand cubic feet, independently of the quality of the gas. If the calorific value is 500 B.Th.U.'s per cu. ft., then 1000 cu. ft. = 5 therms. The price per therm, of course, varies. The gas company may declare the calorific value of the gas it supplies, and this is then regularly tested by independent examiners.

The oxygen, which is equally as essential as gas or coal in producing heat, is supplied free in the atmosphere.

## OZONE

**Ozone.**—The invigorating properties of sea air are popularly attributed to 'ozone,' and this substance is produced by electric discharges in the atmosphere, and especially by the action of ultra-violet light from the sun on the oxygen in the upper layers of the atmosphere. Normal air contains about  $10^{-8}$  per cent. by volume of ozone (Paneth, 1938).

Van Marum in 1785 noticed that the air in the vicinity of an electrical machine in active operation acquires a peculiar smell, and tarnishes mercury. This smell is easily noticed in a physics laboratory when experiments on electrostatics are in progress. Cruickshank in 1801 observed the same smell in electrolytic oxygen, but the fact that the odour is due to a peculiar gas was only recognised in 1840 by Schönbein, who gave the substance the name **ozone** (Greek *ozo*, I smell). He found that it is also produced by the slow oxidation of phosphorus in moist air, and is capable of liberating iodine from potassium iodide.

A few sticks of freshly scraped phosphorus are placed in a stoppered bottle with a little water. When the fumes have subsided, a piece of paper dipped into a solution of potassium iodide and starch ('starch-iodide paper') introduced into the bottle is turned blue. The peculiar smell of the gas is also noticeable.

Ozone is a powerful oxidising agent. It is difficult to obtain pure, when it is very explosive, but a mixture of ozone with oxygen or with air is easily made by the action of a 'silent electric

discharge' on these gases. The best apparatus for the experiment is Brodie's ozoniser (Fig. 190).

The oxygen or air is passed slowly through the annular space between two glass tubes, the inner tube being filled with dilute sulphuric acid or copper sulphate solution, and the whole apparatus placed in a jar of the same liquid. The two wires from a coil dip into the two liquids, which form electrodes, and at the same time serve to cool the apparatus. A bluish-violet glow is seen in the glass surfaces, accompanied by a hissing noise; there should be very few sparks, as these destroy ozone. The gas is conducted away through glass tubes with ground-glass joints, or joints of ordinary corks. Rubber is very quickly destroyed by ozone.

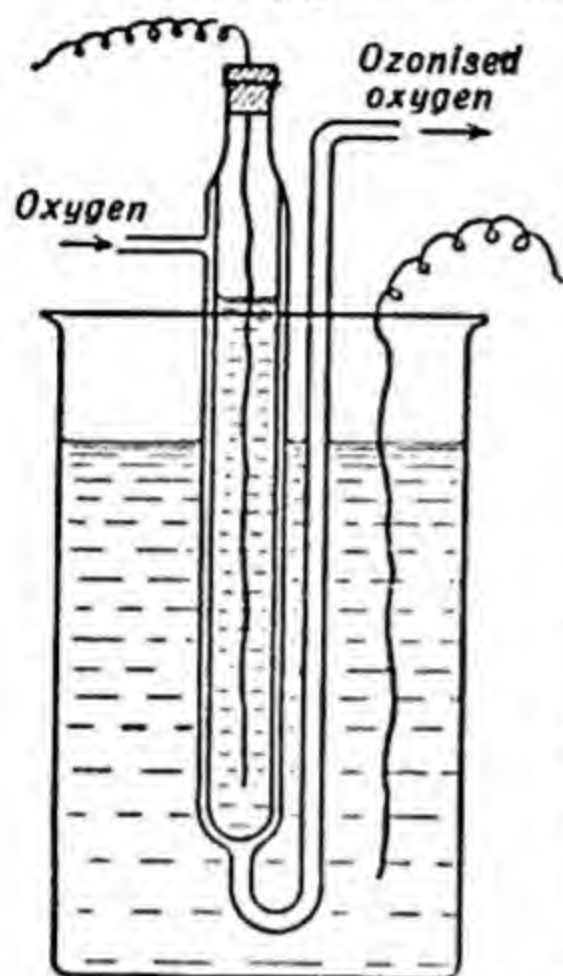
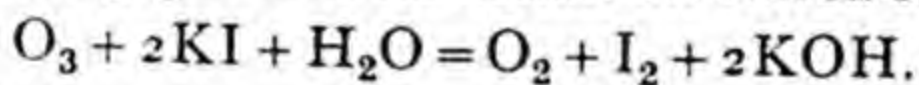


FIG. 190.  
BRODIE'S OZONISER.

Siemens' ozoniser (Fig. 191) consists of two concentric glass tubes, the outer covered, and the inner lined, with tinfoil to form the electrodes.

The formation of ozone in the apparatus is detected by the smell of the issuing gas and its action on starch-iodide paper :



Only one of the oxygen atoms in the ozone molecule oxidises the iodide: the other two appear as a molecule of ordinary

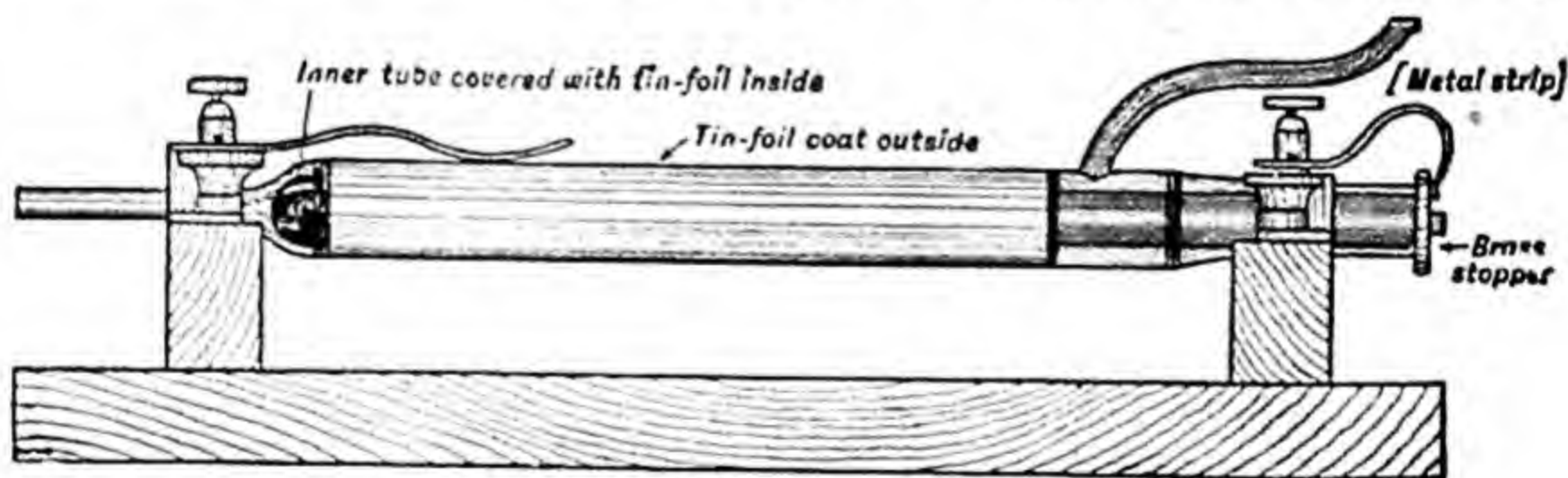
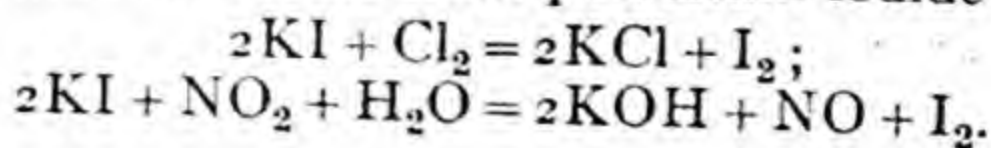


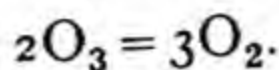
FIG. 191.—SIEMENS' OZONISER.

oxygen. Chlorine, hydrogen peroxide (*q.v.*), and oxides of nitrogen also liberate iodine from potassium iodide :



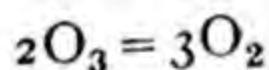


When the gas coming from the ozoniser is passed through a heated glass tube, all the ozone is converted into oxygen :



Ozonised air is used for sterilising water, and has also been used in removing unpleasant odours from air in confined spaces, *e.g.*, underground railways. A curious use of ozone is in the conversion, by oxidation, of oil of cloves into *vanillin*, the material which gives the odour and flavour to vanilla, and is used instead of the natural material in flavouring custards, chocolate, etc. This artificial vanillin is made on a large scale at Niagara.

The formula of ozone,  $\text{O}_3$ , was found by Soret. If we suppose the whole of the ozone present in a given volume of ozonised oxygen to be absorbed by oil of turpentine (which absorbs ozone *in toto*), and if we then suppose the ozone contained in another equal volume of the same ozonised oxygen decomposed by heat, the equation



shows that if the formula of ozone is  $\text{O}_3$ , the contraction on absorption is twice the expansion on heating.

Instead of measuring the *expansion* when ozone is converted into oxygen on heating, we may measure the *contraction* of a given volume of oxygen when it is ozonised, and then, by introducing turpentine into the resulting gas, measure the further contraction which occurs when the ozone is absorbed by the turpentine.

The apparatus shown in Fig. 192 consists of two concentric glass tubes, the inner tube fitted into the outer by a ground-glass joint. The inner tube contains dilute sulphuric acid, and the apparatus, previously filled with dry oxygen, is supported in a jar of water and crushed ice. Two wires from the coil dip into the liquids. By means of projections from the inner and outer tubes a thin glass tube containing turpentine is held in position

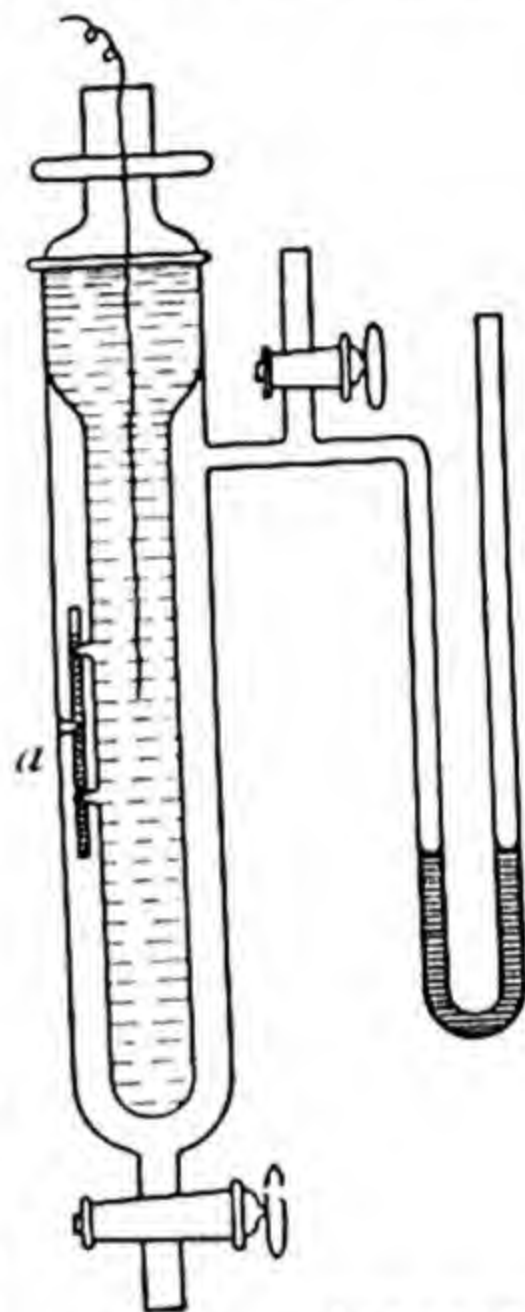


FIG. 192.—APPARATUS FOR DETERMINING THE FORMULA OF OZONE.

in the annular space. The manometer, containing concentrated sulphuric acid coloured with indigo, is in communication with the apparatus. The levels are adjusted, and the oxygen is ozonised. The contraction, after cooling, is read off on the gauge. The inner tube is then twisted, so as to break the tube of turpentine, and after absorption is complete and the original temperature is restored, the further contraction is read off. It will be found that the contraction on absorption is twice the contraction on ozonisation.



## CHAPTER XVII

### HYDROGEN

**History.**—Hydrogen gas ( $H_2$ ) was probably first prepared by Boyle from steel filings and hydrochloric acid, as well as from iron nails and dilute sulphuric acid, although Van Helmont (1648) had described an inflammable gas (*gas pingue*). It was carefully investigated by Cavendish in 1766 and called by him *inflammable air*.

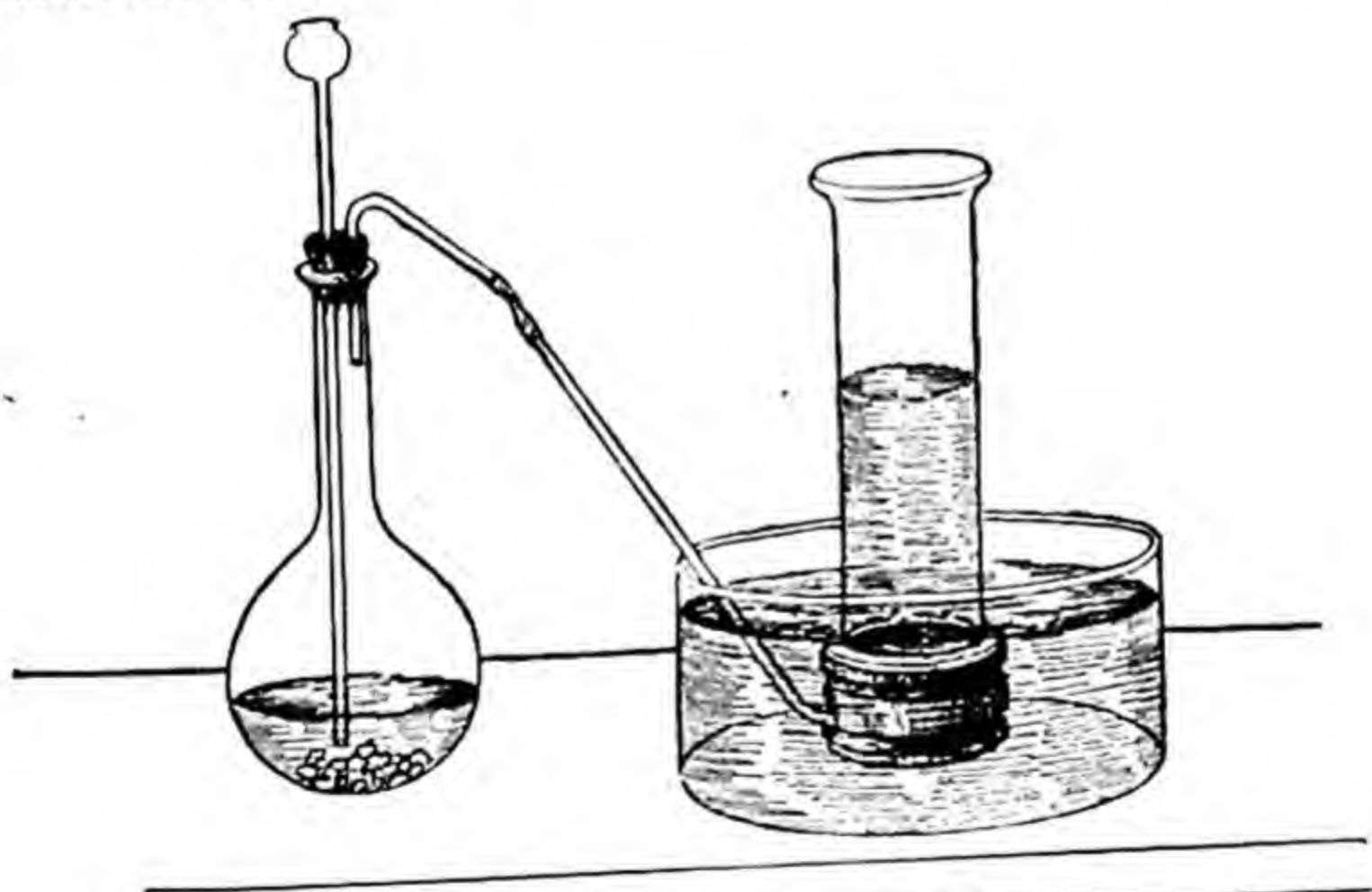
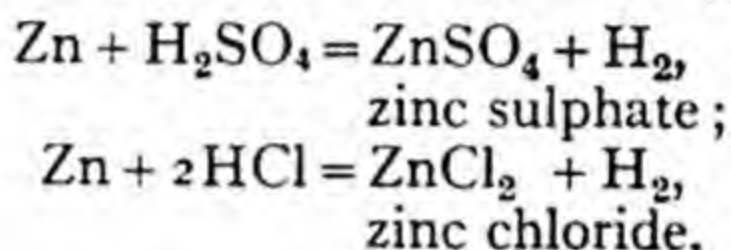


FIG. 193.—PREPARATION OF HYDROGEN.

**Occurrence.**—Hydrogen is said to occur in the free state in some volcanic gases, and the outer atmosphere of the sun is found by spectrum analysis to consist largely of hydrogen. Hydrogen is found in most specimens of meteoric iron. The artificial products coal gas and water gas contain large amounts of free hydrogen.

Hydrogen in combination is more common. With oxygen it forms water,  $\text{H}_2\text{O}$ ; with sulphur, sulphuretted hydrogen,  $\text{H}_2\text{S}$ , and with carbon it forms a large number of compounds called hydrocarbons, which make up petroleum. All organic substances, of which vegetable and animal tissues are composed, contain hydrogen, and this element is an essential constituent of acids and alkalies.

**Preparation.**—The usual *laboratory* method of preparation of hydrogen is to act upon granulated zinc in a flask or Woulfe's bottle with dilute sulphuric acid (1 vol. conc. acid to 5 vols. water) or dilute hydrochloric acid (1 vol. conc. acid to 4 vols. water), poured in through a thistle funnel (Fig. 193):



The zinc salts remain in solution in the flask; the hydrogen is collected over water. Instead of a flask, Kipp's apparatus

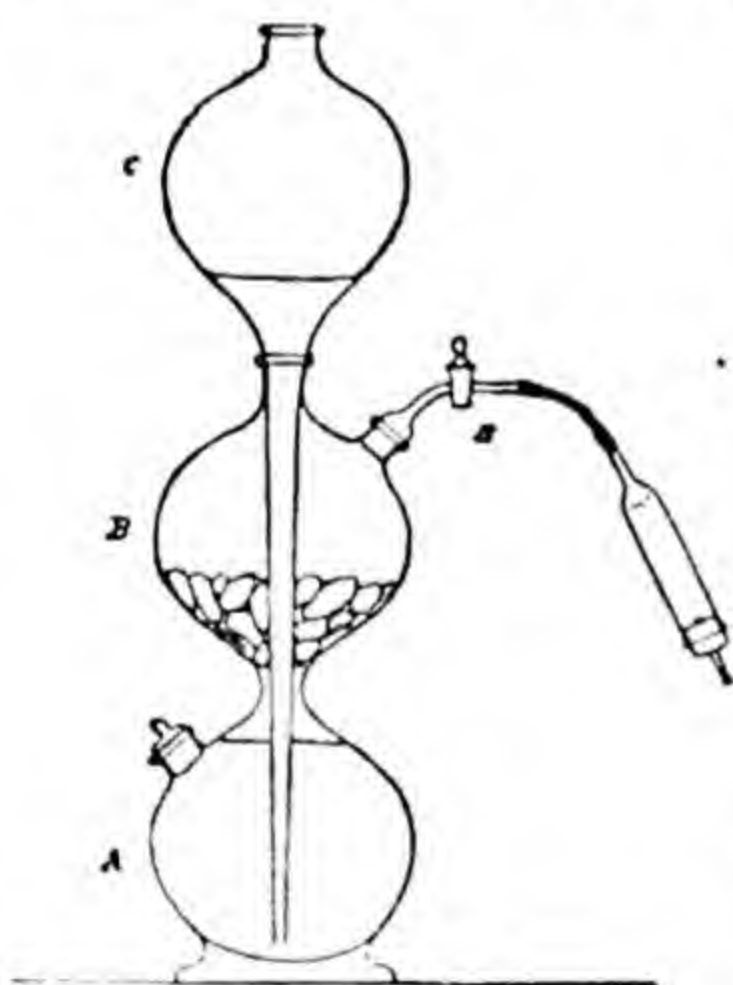


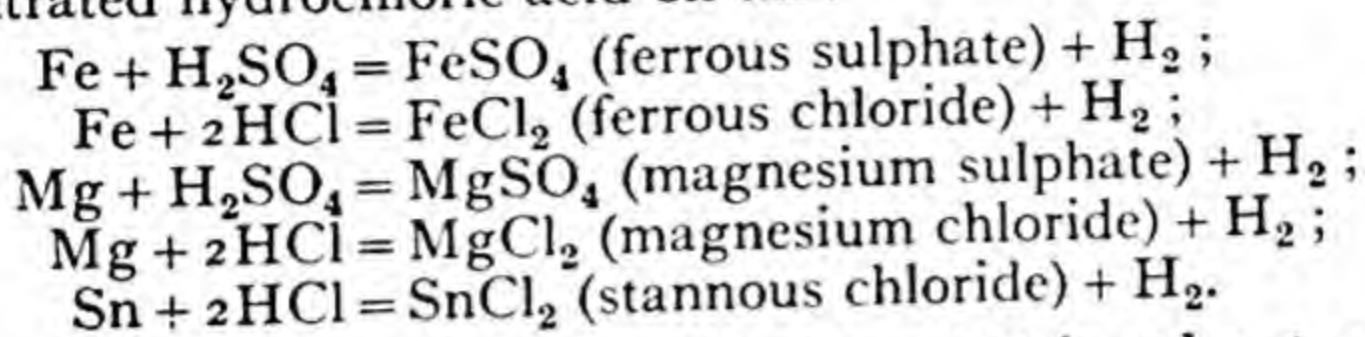
FIG. 194.—KIPP'S APPARATUS.

(Fig. 194) may be used, the metal being placed in the central globe *B* and acid poured in the top funnel until the lower bulb *A* is full, and the metal covered with acid. When the tap *E* is closed evolution of gas continues until the liquid is forced by pressure partly into the upper globe, and the metal is brought out of contact with the liquid, when the action ceases.

The Kipp's apparatus may be used for the generation of gas from any liquid reagent and a solid which can be obtained in the form of lumps which do not disintegrate in contact with the liquid, e.g., carbon dioxide from marble and hydrochloric acid, and sulphuretted hydrogen from ferrous sulphide and hydrochloric acid. Since hydrogen is very much lighter than air it may also be collected by upward displacement (Fig. 195). It may be dried by calcium chloride.

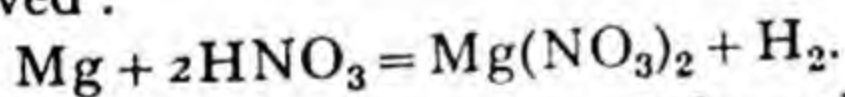


Hydrogen is also liberated by the action of dilute hydrochloric or sulphuric acid on iron (which gives a rather impure gas with an unpleasant odour) or magnesium, or by the action of hot concentrated hydrochloric acid on tin :



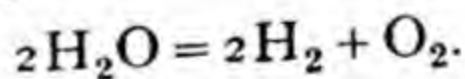
*Before collecting hydrogen great care must be taken to ensure that all the air has been displaced from the apparatus, since a mixture of hydrogen with air is explosive.* A little of the gas is first collected in a test-tube and a flame applied: the gas in the tube should burn slowly and quietly, and not explode. (The mere absence of explosion is misleading, since the first portion of gas collected may be air: the gas following this is highly explosive.)

Copper and lead are not dissolved by acids with evolution of hydrogen, and the action of nitric acid on metals nearly always gives oxides of nitrogen, not hydrogen (p. 390). With magnesium and *very dilute* nitric acid, hydrogen is evolved :



Vague general statements, such as that 'hydrogen is formed by the action of acids on metals,' are useless in chemistry.

**Hydrogen from water.**—Hydrogen is produced from water by electrolysis (p. 110) :



The metals potassium, sodium, and calcium liberate hydrogen from water, the action of the first two being violent but that of calcium is slow. The heat set free by the action of potassium on water sets fire to the hydrogen, which burns with a lilac-coloured flame. Sodium amalgam, obtained by dissolving sodium in mercury, decomposes water quietly :

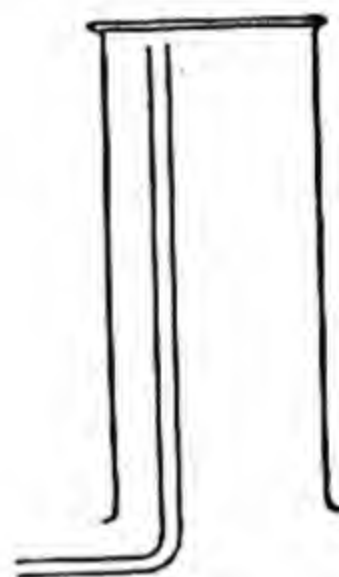
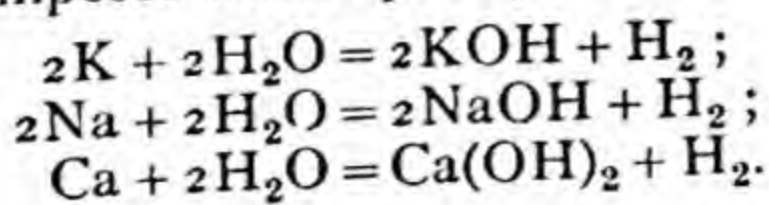
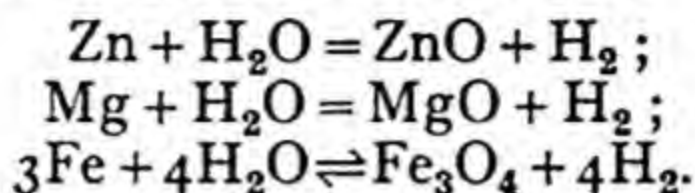
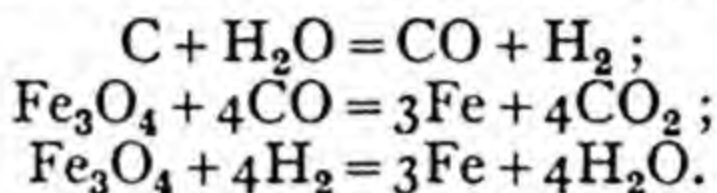


FIG. 195.—COLLECTING HYDROGEN (OR OTHER LIGHT GASES) BY UPWARD DISPLACEMENT.

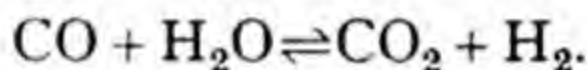
Iron, zinc, and magnesium decompose steam when heated in it :



The preparation of hydrogen from steam and iron has been described on p. 109. The process is used on the technical scale, the oxide of iron formed being reduced by **water gas**, containing hydrogen and carbon monoxide, formed by passing steam over red-hot coke :

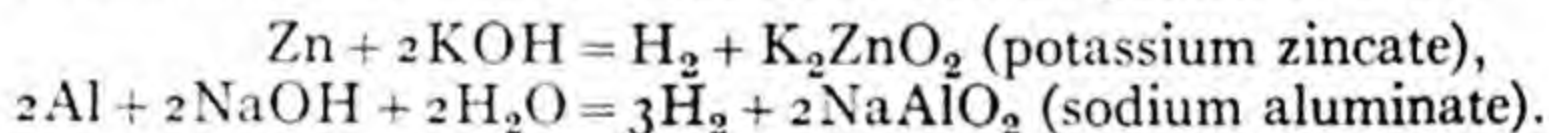


In another technical process hydrogen is obtained from water gas itself, which is mixed with steam and passed over a catalyst composed of ferric oxide containing nickel and chromium oxides which increase the activity of the iron oxide and are called **promoters**. The reaction is :

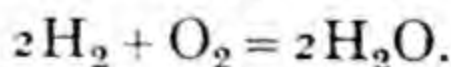


The carbon dioxide is removed from the gas by washing with water under pressure. Immense quantities of hydrogen are prepared in this way for the production of synthetic ammonia (p. 379).

Hydrogen may also be prepared in the laboratory by heating zinc or aluminium with a solution of caustic potash or soda.



**Properties of hydrogen.**—Hydrogen is a colourless gas which when pure has no smell or taste. It does not support respiration although it is not poisonous. Hydrogen is the lightest gas known, and is used in **balloons** and **airships**, although its inflammability makes it dangerous for this purpose. Coal gas, which contains hydrogen, is often used in balloons, and helium, the next lightest gas to hydrogen, is used instead in airships in America (p. 400). Considerable quantities of hydrogen are used in making solid fats from oils (**oil hardening**). Hydrogen burns in oxygen or air, forming water :

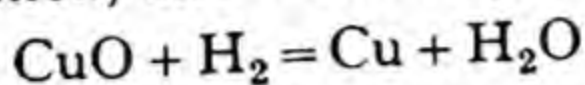


It does not support the combustion of a taper, as may be seen by passing a lighted taper into an inverted jar of hydrogen. A jet of oxygen, however, will burn in hydrogen (p. 282). A



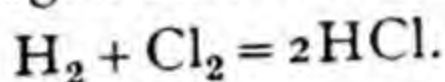
mixture of hydrogen with oxygen or air explodes violently when ignited (provided either gas is not in too great excess), water being formed.

By reason of its tendency to unite with oxygen, hydrogen acts as a **reducing agent**. Thus, if hydrogen is passed over many heated metallic oxides (copper, iron, lead), the latter are reduced to the metallic condition, and water is produced :

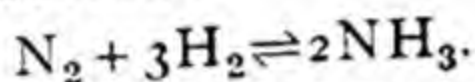


(*cf.* p. 113). Some oxides, *e.g.*, zinc and aluminium oxides, are not reduced by hydrogen.

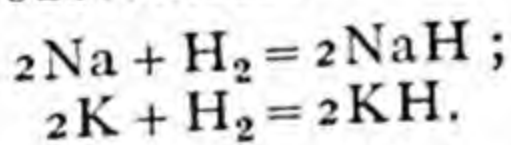
Hydrogen burns in chlorine, and a mixture of hydrogen and chlorine explodes violently when ignited or when exposed to bright sunlight. Hydrogen chloride is formed :



Hydrogen will unite with nitrogen in presence of a catalyst, ammonia gas being produced :

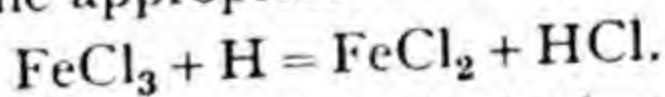


Hydrogen combines with heated sodium or potassium, forming sodium or potassium hydride. These compounds when pure are colourless salt-like substances :



Hydrogen is absorbed or occluded by the metal palladium (p. 116). In this case also a hydride,  $\text{Pd}_2\text{H}$ , seems to be formed.

**Active or nascent hydrogen.**—If a little ferric chloride is added to a mixture of zinc and dilute sulphuric acid which is evolving hydrogen, the ferric salt is rapidly reduced to a ferrous salt, as may be found by the appropriate tests :



No such change is produced by bubbling gaseous hydrogen through the solution.

It is supposed that the peculiar activity of the hydrogen in such cases is due to the fact that it is **nascent** (new-born), *i.e.*, in the act of liberation from its compounds, and that the nascent condition is due to the hydrogen being then in the state of *free atoms*, which had not time to join up to form molecules before interaction occurred.

Nascent hydrogen is also formed at the cathode in electrolysis ; the hydrogen ions are deposited as atoms.

**Catalytic combustion.**—Although oxygen and hydrogen do not combine at the ordinary temperature, a jet of hydrogen is inflamed if directed on a little platinum sponge. The same effect is produced by a bundle of fine platinum wires, which become red-hot and then kindle the hydrogen (Döbereiner, 1823). This is a catalytic action (p. 275).

Döbereiner's lamp (Fig. 196) is a small hydrogen generator. A glass tube, with a stopcock and jet at the top, is held in dilute sulphuric acid. A piece of zinc hangs inside the tube, and the gas generated displaces the acid until it is no longer in contact with the zinc, when action ceases. Opposite the jet is a sponge of fine platinum wire enclosed in a brass tube, and when the tap is opened the stream of hydrogen ignites. This property has been applied in automatic gas lighters, which contain fine platinum wires in a perforated brass tube. The wire fairly soon loses its activity.

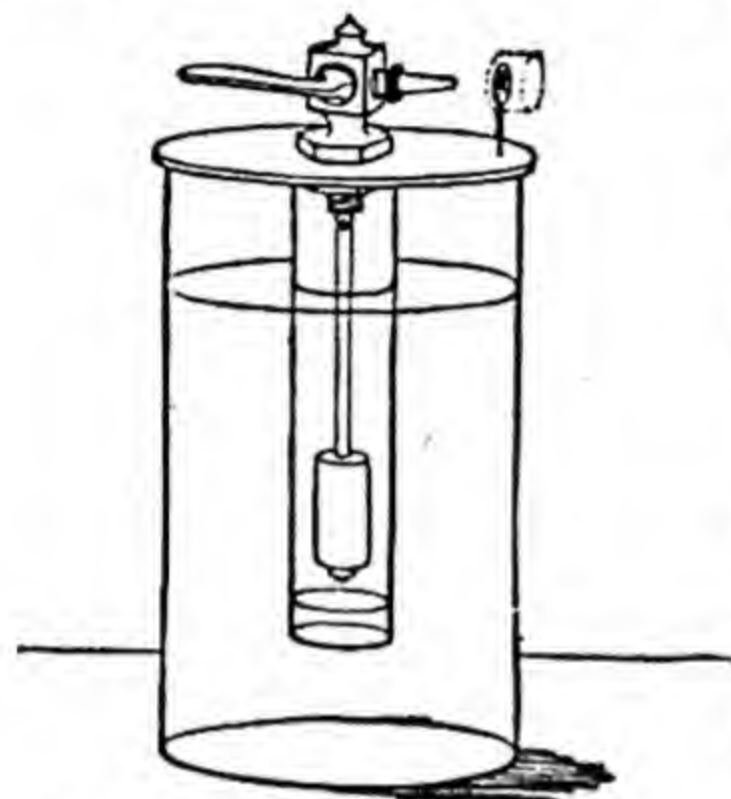


FIG. 196.—DÖBEREINER'S LAMP.

**\*Atomic hydrogen.**—Langmuir has shown that when hydrogen is

strongly heated, say by contact with a tungsten wire heated by an electric current, and surrounded by hydrogen gas at low pressure, its molecules are dissociated into atoms:  $\text{H}_2 \rightleftharpoons 2\text{H}$ . This splitting of the hydrogen molecule is attended by the absorption of a large amount of energy, about 100,000 calories per gram-molecule. The atomic hydrogen so formed is chemically very active. Langmuir also showed that atomic hydrogen is formed when an electric arc between tungsten electrodes is allowed to burn in hydrogen at atmospheric pressure (Fig. 197). The atomic hydrogen was blown out of the arc by a jet of molecular hydrogen directed across the arc, and formed an intensely hot flame, which is capable of melting tungsten (m.pt.  $3400^\circ$ ). This flame obtains its heat not from combustion but from the recombination of hydrogen atoms to  $\text{H}_2$ . It is suitable for melting and welding many metals. Iron can be melted without contamination with carbon, oxygen, or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminium, silicon, or manganese



can be melted without fluxes and without surface oxidation. A feature of the flame is the great rapidity with which heat can be delivered to a surface, which is very important in welding operations. Whereas an ordinary blast-lamp burning gas and

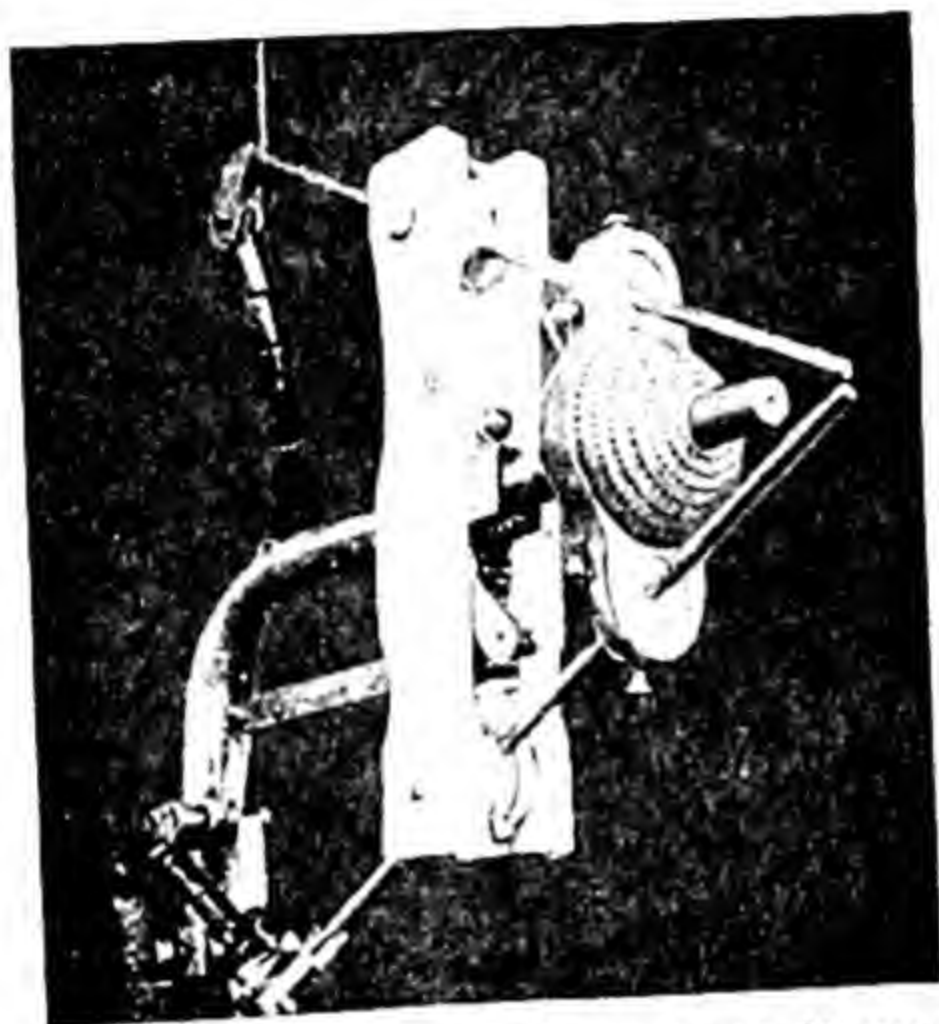


FIG. 197.—THE ATOMIC HYDROGEN BLOWPIPE.  
HYDROGEN GAS ISSUES FROM THE CENTRAL NOZZLE ON THE RIGHT AND IS DISSOCIATED IN AN ELECTRIC ARC BETWEEN TWO TUNGSTEN RODS NEARLY MEETING IN A V.

air delivers about 57 watts per sq. cm., the atomic hydrogen flame can deliver over 1000. It is curious that quartz is very difficult to melt: although it evaporates rapidly in the flame, it does not melt to a mobile liquid but remains viscous.

## CHAPTER XVIII

### COMPOUNDS OF HYDROGEN AND OXYGEN

Hydrogen and oxygen form two compounds :

water,  $\text{H}_2\text{O}$  (hydrogen monoxide) ;  
hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

**Water.**—The history of the discovery of the composition of water has been fully described in Chapter VI. The occurrence of water is too well known to need description, and its preparation simply involves the purification of a natural water by distillation (p. 32). We may, therefore, pass at once to a consideration of the properties of water.

**The physical properties of water.**—Water exists in three states of aggregation: solid (ice), liquid (water), and vapour (steam). What is ordinarily called 'steam' is not true water vapour, which is invisible, but a mist of small droplets of liquid water.

If water is boiled in a flask fitted with a short bent tube, a cloud of 'steam' issues from the tube, but the interior of the flask, which is filled with true water vapour is quite clear. If a Bunsen flame is held below the delivery tube, the mist disappears. A short distance from the tube is also seen to be clear in the first part of the experiment. This consists of vapour which has not cooled to the condensing point.

Liquid water possesses a faint though distinct blue colour, which is seen when light is passed through a long tube of water closed at the ends with pieces of plate glass. Ice also shows the same colour in large masses, as in the crevices of glaciers or ice-floes. The deep blue colour of certain clear lakes, however, appears to be due to light scattered from fine particles of solid matter in suspension.

The expansion of water by heat is peculiar. From  $0^\circ$  to  $4^\circ$ , the liquid *contracts*; beyond  $4^\circ$  it expands. Thus, at  $4^\circ$  water is in a state of **maximum** density, and then expands either on heating or on cooling. Owing to this property, exposed water



freezes only on the surface ; the water sinks as it reaches  $4^{\circ}$ , and forms a heavier layer beneath the upper crust of ice, through which heat is only very slowly transmitted.

It is not only in this respect that water is abnormal : it is, in nearly all its properties, one of the most abnormal substances known to the chemist.

The density of ice is lower than that of water, so that ice floats on water, and water expands on freezing. Water pipes are burst on freezing ; the result is obvious when a thaw sets in. Cast-iron bottles filled with water and closed with screw plugs are burst when immersed in a freezing mixture. The formation of ice in the crevices of rocks assists in the gradual disintegration of the latter, and the freezing of water in the cylinder jackets and radiators of automobile engines leads to cracks and damage.

Ice crystallises in the hexagonal (six-sided) system. Beautiful crystals are seen (Fig. 198) when snowflakes are examined on a cold slide under the microscope. The bubbles in ice are composed of air which was dissolved in the water, and is liberated

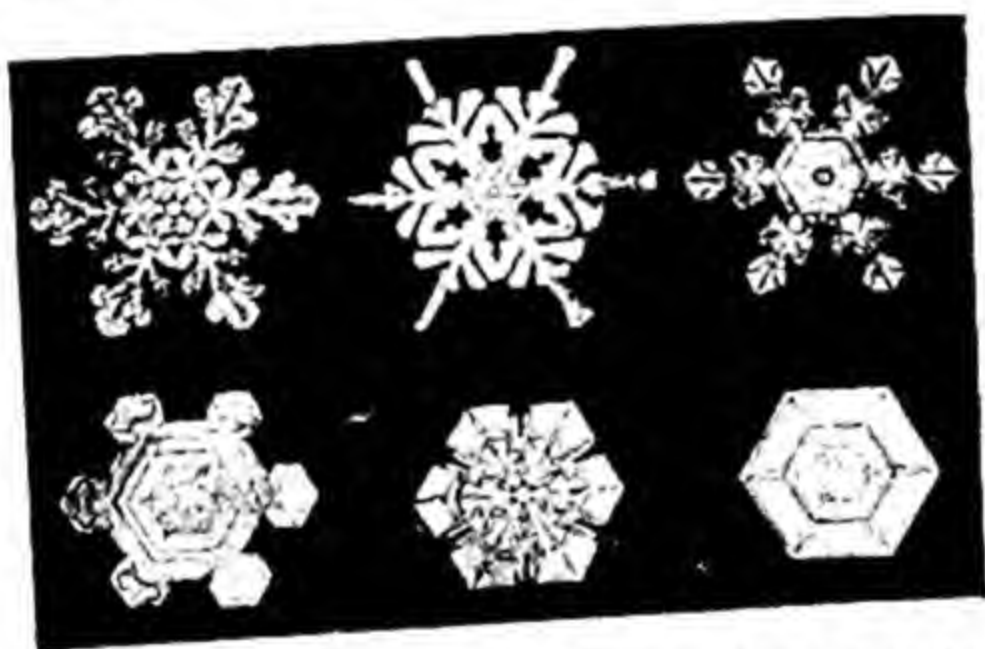


FIG. 198.—FORMS OF SIX-SIDED (HEXAGONAL) ICE CRYSTALS.

on freezing. In making clear ice, the freezing is carried out slowly, with agitation, so that the air bubbles have an opportunity to escape. Rectangular tanks filled with water are immersed in a large tank through which a cold solution of calcium chloride ('brine'), which does not freeze until  $-30^{\circ}$ , is circulated from a refrigerating machine (p. 380).

**Pure water.**—There is probably no substance more difficult to obtain in a state of extreme purity than water. It is a close approach to the *alkahest*, or universal solvent, of the alchemists, since it dissolves traces of practically everything with which it

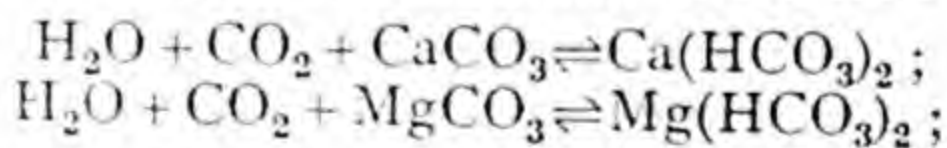
is brought in contact. For chemical purposes, water is purified by distillation, preferably in a copper vessel with a copper or pure tin condenser. Distilled water, which is made on board ship, has an unpleasant 'flat' taste: for drinking purposes it is aerated and small amounts of certain salts added to it.

**Natural waters.**—Water as it occurs in Nature contains various impurities, present in amounts varying considerably with the particular source of the water. The following division of natural waters is convenient: (1) rain water, (2) river water, (3) spring, or deep well, water, (4) sea water, and (5) mineral waters.

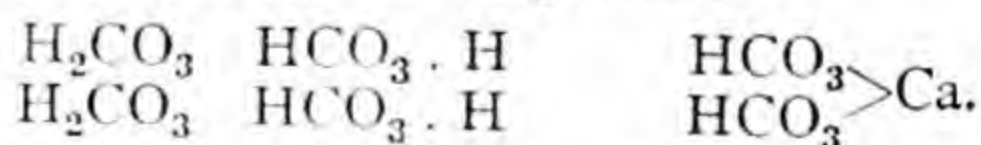
The impurities in natural water are of two kinds: (1) suspended impurities, both mineral and organic; (2) dissolved impurities, both solids (mineral and organic), and gases.

**Rain water** always contains impurities, especially if it is deposited in the neighbourhood of towns where coal is burnt. Dissolved atmospheric gases (oxygen, nitrogen, carbon dioxide), and sodium chloride, derived from sea spray carried inland by winds, are invariably present. Nitrous and nitric acids, produced by electrical discharges (lightning), are nearly always present in the forms of ammonium nitrite and nitrate, and sometimes free ammonia occurs. In the vicinity of towns, sulphuric acid, from the sulphur dioxide formed by the combustion of coal (which contains iron pyrites,  $\text{FeS}_2$ ), is present. The suspended impurities, chiefly soot from fuel smoke, are contained in larger amounts in rain falling near towns.

**River water** is rain water which has percolated through the surface soil, and taken up salts, organic matter, and suspended matter, such as clay. The dissolved matter is especially marked when the water has passed through limestone or calcareous soil (*i.e.*, soil rich in calcium carbonate), because the carbonic acid present in the rain, produced from atmospheric carbon dioxide,  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ , dissolves the carbonates of calcium and magnesium, forming unstable soluble bicarbonates:



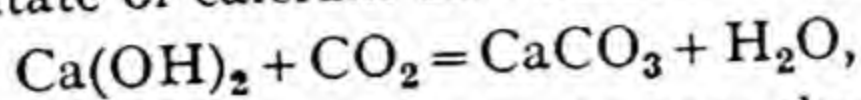
which are derived from two molecules of carbonic acid in which one hydrogen atom from each molecule has been replaced by the bivalent metal, calcium or magnesium:



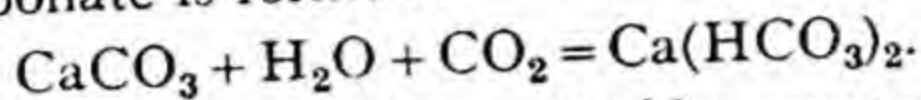
**Temporarily hard water.**—The formation of calcium bicar-



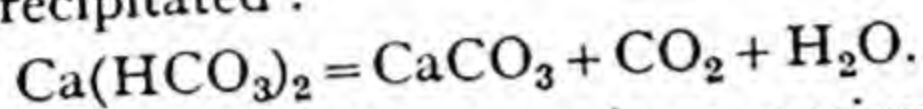
bonate is shown by passing a slow current of carbon dioxide through clear lime water (a solution of calcium hydroxide). A white precipitate of calcium carbonate is first produced :



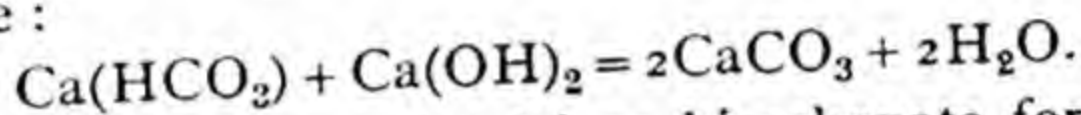
but as the carbon dioxide continues to pass through the liquid, this precipitate gradually dissolves, and a clear solution of calcium bicarbonate is formed :



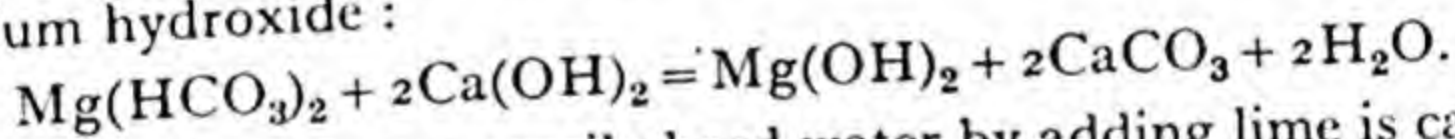
On *boiling* the solution, carbon dioxide escapes and calcium carbonate is precipitated :



**Hard water** containing calcium and magnesium bicarbonates therefore deposits a 'scale' or 'fur' of calcium and magnesium carbonates in kettles or boilers. Such water, which is softened by boiling, is called **temporarily hard water**. It may be softened by adding just enough lime water to precipitate the calcium bicarbonate :

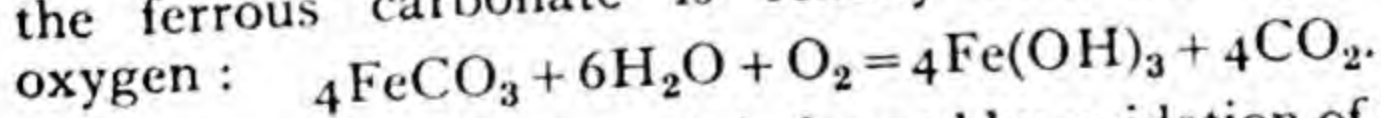


If, to the clear solution of calcium bicarbonate formed in the above experiment, an equal volume of lime water is added, a white precipitate of calcium carbonate is formed. Since magnesium carbonate is rather soluble, enough lime water is added to precipitate the magnesium bicarbonate, if present, as magnesium hydroxide :



The softening of temporarily hard water by adding lime is called **Clark's process**.

Ferrous carbonate also dissolves in water containing dissolved carbon dioxide (carbonic acid), forming ferrous bicarbonate,  $\text{Fe(HCO}_3)_2$ . On boiling, or exposure to air, a reddish-brown precipitate of ferric hydroxide,  $\text{Fe(OH)}_3$ , is thrown down, since the ferrous carbonate is readily oxidised by atmospheric oxygen :



A similar ochre-like deposit is formed by oxidation of ferruginous water in streams. If such water is used for washing, the slimy calcium salts formed from soap carry down brown ferric hydroxide, which adheres to the fabric in spots, forming 'iron-mould.' Ferruginous waters often occur near coal mines, and the dissolved iron comes from the oxidation of pyrites,  $\text{FeS}_2$ .

Waters containing magnesium and calcium carbonates held in solution by carbonic acid, when they fall in drops from the roofs of caves, lose the carbonic acid by evaporation and deposit the insoluble salts in the form of pendants, made up of several concentric layers, and known as **stalactites** (Fig. 199). The



(Photo: Frith & Co. Ltd.)

FIG. 199. STALACTITES AND STALAGMITES IN COX'S CAVE, CHEDDAR.

drops falling on the floor of the cave also deposit salts, and another concretion called a **stalagmite**, growing upwards to meet the stalactite, is formed. Small stalactites are formed under brickwork arches even in localities where the water is soft. These are derived from the calcium carbonate in the mortar, which is dissolved by the carbon dioxide in rain water.

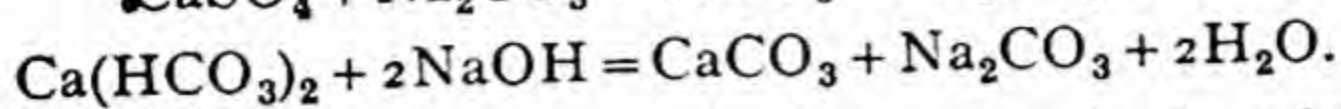
Temporarily hard waters cause waste of soap, since they precipitate the sodium salts of fatty acids in the soap in the form of calcium and magnesium salts, which also carry down some soap with them.

#### **Permanently hard water.—**

A different kind of hardness is that due to the presence of the sulphates or chlorides of calcium and magnesium, derived from the soil. These

are not precipitated on boiling, and cause **permanent hardness**. The water may, in addition, possess temporary hardness. If such waters are evaporated in boilers, calcium sulphate is deposited as a very hard, crystalline scale, which may impede the transmission of heat. Such waters cause waste of soap in laundry work for the same reason as temporarily hard water. Permanently hard waters are softened, for example, for use in laundries or in steam boilers, by adding a mixture of caustic soda and sodium carbonate, when both temporary and permanent hardness are removed:





Other chemicals used for softening water in laundries are ammonia ( $\text{NH}_4\text{OH}$ , which acts like caustic soda), and borax, which precipitates calcium borate.

A method of softening water is Gans' **permutit process**. Permutit is a silicate of sodium and aluminium allied to the natural mineral zeolites. On percolating hard water through it, the calcium and magnesium salts in the water are removed and replaced by an equivalent of sodium salt. The change is reversible, and the permutit is re-activated by percolation with a solution of common salt.

Hardness in drinking water is not known to be injurious: the bicarbonates give the water a refreshing taste and prevent its action on lead pipes.

**River water.**—River water, which has previously percolated through soil, contains dissolved salts and suspended matter, both mineral (clay) and organic, from vegetable matter. Water which has flowed over peat, or peaty soil, contains dissolved organic acids, which give it a yellow colour, and cause it to corrode lead or iron pipes.

River water flowing over cultivated land contains, in addition to the above impurities, ammonium salts, nitrites, nitrates, sodium chloride, and organic matter of vegetable and animal origin containing nitrogen. The purity of the water depends on the nature of the soil. Thames water, flowing over soil rich in limestone, contains about 157 milligrams of calcium carbonate per litre. Trent water, flowing over soil containing gypsum, contains 300 milligrams of calcium sulphate per litre. The waters of the Dee and Don, draining the Aberdeen granite area, contain only traces of dissolved calcium salts.

**Spring, or deep well, water** differs from river water only in having undergone filtration through porous strata. In this way the suspended matter may be largely removed, leaving the water clear. The organic matter and nitrites may also have been more or less oxidised, but the dissolved mineral impurities usually increase. Of 100 parts of rain, only 36 flow to the sea in rivers; the rest is either evaporated, or penetrates into the earth's crust, to reappear to some extent in springs. This type of natural water is probably the best for drinking purposes.

It is very important that drinking water shall not contain disease germs, so that it is now often **sterilised**. This is effected

by means of ozone (p. 287), or more usually by adding small quantities of chlorine or bleaching powder solution, which are powerful germicides. Free exposure to air and sunlight also causes sterilisation. Water for drinking purposes is usually filtered by passing it through layers of sand or porous material.

**Sea water.**—Sea water contains a large proportion of dissolved solids, about 3·6 per cent. on the average, of which 2·6 per cent. represents sodium chloride. Sea water also contains bromides and iodides, and bromine is now extracted from it (p. 331).

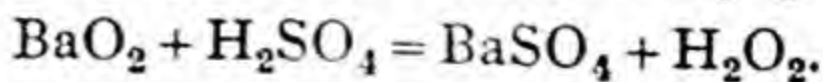
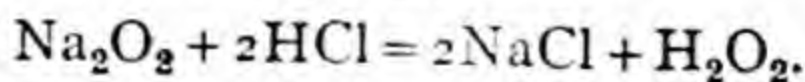
**Mineral waters.**—Natural waters containing special constituents not present (except in traces) in ordinary water are known as mineral waters. They are of seven kinds, according as the principal constituent is carbon dioxide, ferrous carbonate held in solution by carbon dioxide (*chalybeate waters*), sulphuretted hydrogen (*hepatic waters*), alkalies, magnesium or sodium sulphates, silica, or iodides. Artificial mineral waters are made by dissolving salts in water and impregnating with carbon dioxide under pressure (*e.g. soda water*).

**Hot springs** occur in various places, *e.g.*, Buxton (28°) and Bath (47°). They often contain dissolved gas, including helium, and traces of radium emanation (p. 253), to which their medicinal properties are attributed.

## HYDROGEN PEROXIDE

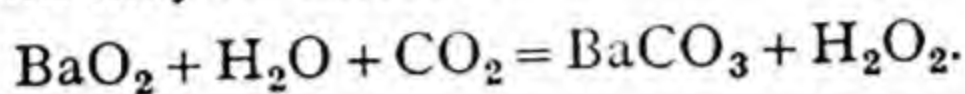
**Hydrogen peroxide.**—The other compound of hydrogen and oxygen, hydrogen peroxide, is unstable and readily decomposes into water and oxygen:  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ ; it is used either in solution, or freshly liberated from compounds rich in oxygen, as a disinfecting or bleaching agent, the effects being produced by the oxygen liberated from the compound (*nascent oxygen*). Hydrogen peroxide was discovered by Thenard in 1818. It occurs in traces in rain and snow, and is formed in small quantities when a hydrogen flame is allowed to play on a piece of ice: the melted ice contains a trace of hydrogen peroxide:  $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ .

Hydrogen peroxide is prepared by the action of acids on sodium peroxide or barium peroxide:

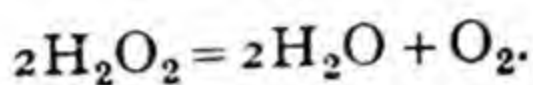




In order to obtain a solution of hydrogen peroxide free from dissolved salts, barium peroxide and dilute sulphuric acid are generally used, the barium sulphate formed being filtered off. Phosphoric acid, which gives insoluble barium phosphate, may also be used, or barium peroxide may be suspended in water and carbon dioxide passed in, when insoluble barium carbonate is produced and may be filtered off:



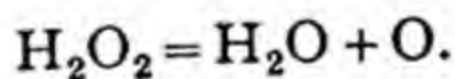
The solution is fairly stable in presence of a trace of acid, but it is decomposed on boiling, or in presence of alkalies, oxygen being evolved:



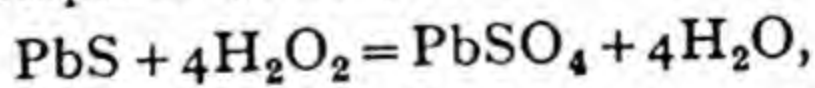
The strength of the solution is often stated in terms of the volume of oxygen produced from 1 volume of solution on boiling, *e.g.*, '10 volumes' and '20 volumes' are common strengths, although '100 volumes' solution is also manufactured.

Pure hydrogen peroxide is a nearly colourless (pale blue) syrupy liquid obtained by distilling the solution under low pressure. Water distils over first, and the later fractions consist of hydrogen peroxide, which may be frozen to obtain it quite pure. The liquid is unstable.

Hydrogen peroxide solutions are often kept in bottles made of brown glass to minimise the action of light, and the cork is first soaked in melted paraffin wax. A space must be left to allow for the oxygen slowly evolved. Hydrogen peroxide is an **oxidising agent**: one atom of oxygen in the molecule is easily split off, leaving water:

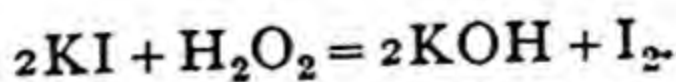


It oxidises lead sulphide (black) to lead sulphate (white):



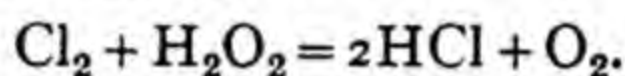
a reaction which is utilised in restoring old oil paintings blackened by exposure, owing to the conversion of white lead (basic lead carbonate) in the pigments to black lead sulphide by traces of hydrogen sulphide in the atmosphere.

Hydrogen peroxide *slowly* liberates iodine from potassium iodide solution:

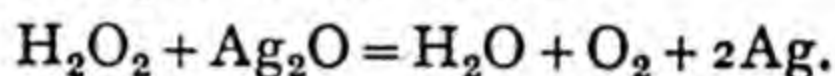


This may be used as a test, the iodine giving a blue colour with starch paste. Another test is the production of a deep blue

solution of perchromic acid in ether when a solution of hydrogen peroxide is shaken with acidified potassium dichromate solution and ether. The ether floats to the top, and if even a trace of hydrogen peroxide is present, a blue colour is noticed. The oxidising action of hydrogen peroxide is used in bleaching delicate materials (wool, silk, ivory, feathers) which would be injured by chlorine : the solution of the peroxide is made faintly alkaline. Hydrogen peroxide bleaches hair to a golden yellow colour. It is a powerful antiseptic, and as it leaves no injurious products after its action, it is largely used as a gargle, etc. Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics :



In certain reactions hydrogen peroxide appears to function as a reducing agent. Thenard (1819) found that gold and silver oxides are reduced by it to the metals :



Hydrogen peroxide forms a stable crystalline compound with urea, called *hyperol*. This liberates hydrogen peroxide when dissolved in water. The solid, which contains 30 per cent. of  $\text{H}_2\text{O}_2$ , is rendered stable by a trace of citric acid.

The structural formula of hydrogen peroxide is  $\text{H} - \text{O} - \text{O} - \text{H}$ .



## CHAPTER XIX

### COMMON SALT. HYDROCHLORIC ACID. CHLORINE

**Common salt.**—It will be convenient to commence the study of the element chlorine by some reference to its best known compound, sodium chloride,  $\text{NaCl}$ , or common salt. After air and water, there is probably no material so familiar as common salt, which is mentioned in the oldest historical records we possess. It is an essential constituent of food, about 29 lb. per head of population being annually consumed in this way. Common salt occurs abundantly, and is very widely distributed in Nature. It is contained in small quantities in all the primary rocks. From these it has passed by the action of water to rivers, and thence to the sea, where the water re-evaporates whilst the salt remains. Average sea water contains about 3 per cent. of salt :

Total percentage of solids	-	-	-	-	3.53
consisting of :					
Sodium chloride	-	-	-	-	76.49
Potassium chloride	-	-	-	-	1.98
Magnesium chloride	-	-	-	-	10.20
Magnesium bromide	-	-	-	-	0.06
Magnesium sulphate	-	-	-	-	6.51
Calcium sulphate	-	-	-	-	3.97
Calcium bicarbonate	-	-	-	-	0.08
					<hr/> 99.29

The extensive deposits of rock salt, found in the earth in many localities, appear to have been produced by the evaporation of former seas and lakes.

**Rock salt**, or **halite**, is the crystalline variety, occurring either as cubic crystals, colourless when pure but often tinged yellow, brown, or sometimes blue, by impurities, or else in large more or less coloured masses, which have a cubic cleavage. The

richest English deposits are in the Cheshire district, at Northwich and Winsford.

Besides rock salt, there are brine springs, yielding a nearly saturated solution of salt. From this brine, salt was prepared by the Romans during their occupation of Britain, by evaporation in square lead pans holding a few gallons. Fig. 200 shows two ancient 'leads' or salt pans excavated in Northwich.



FIG. 200.—ROMAN LEAD SALT PANS.

When discovered there were four; unfortunately the others were broken up and sold for old lead. One fragment recovered from a marine store dealer, bears upon it in large letters, DEVE, the Roman name of Chester, probably indicating that these particular salt pans were the property of the 20th Legion stationed there. The larger pan measures 3 feet 5 inches long, 2 feet  $3\frac{1}{2}$  inches in breadth, and has an inside depth of 4 inches; the lead itself is about  $\frac{1}{2}$  inch in thickness. No other similar pans have ever been found.

Fig. 201 shows miscellaneous objects, viz. a wooden shovel,



scrapers, etc., excavated near the salt pans, and used by the Romans. In the upper part of the illustration are shown two wicker baskets or 'barrows,' used many generations ago in the manufacture of salt. They were filled with salt freshly taken from the pans, and the 'leach,' or waste brine drained away, leaving the pure salt in the 'barrow.' The smaller 'barrow' was used for carrying the salt, when sold in the various markets of the country. The art of 'barrow making' has now entirely died out in Cheshire. The two illustrated are the only ones known to exist, and were specially made, nearly

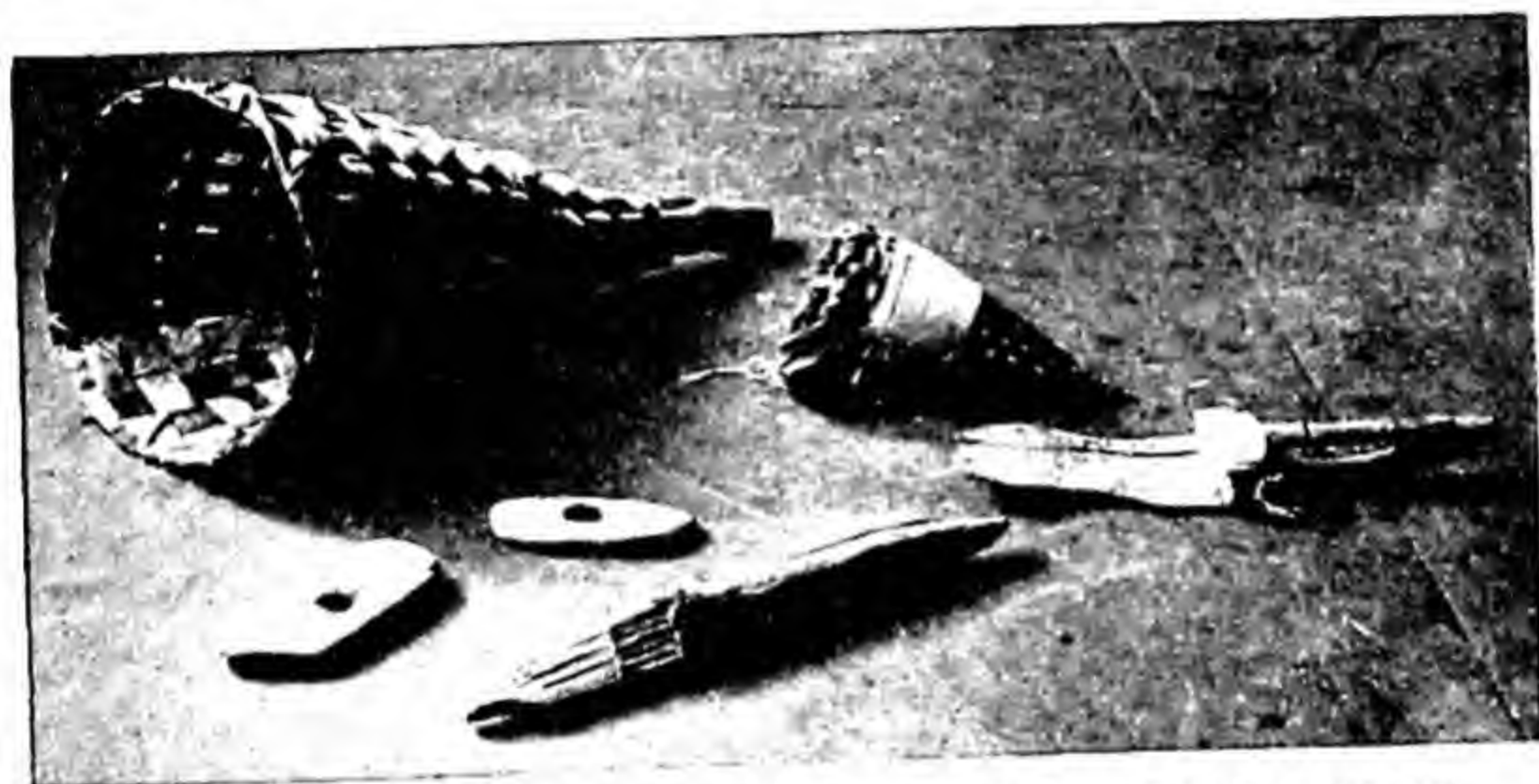


FIG. 201.—TWO WICKER 'BARROWS' FORMERLY USED IN SALT MANUFACTURE, AND ROMAN SALT-MAKING IMPLEMENTS FOUND AT NORTHWICH.

half a century ago, by the last known 'barrow maker.' The use of the 'barrows' is shown in Fig. 202.

With the difference that flat iron pans holding several thousand gallons of brine are now used, the modern process of salt manufacture in Cheshire remains the same. The brine is tapped by bore-holes sunk through the marl; if no brine is found, water is poured down, becomes nearly saturated with salt, and is pumped directly to the evaporating pans. Large cavities are formed by the dissolving out of the salt deposits, and serious subsidences of land often occur.

The more slowly the evaporation proceeds, the larger are the crystals deposited in the pans. The different grades, according to fineness, are: **fine, or table, salt**; **manufacturer's salt**; **fishery salt**, and **bay salt** (usually in the form of floating 'hoppers,' or

cubes with hollow faces). In some works the brine is evaporated in **vacuum pans** under reduced pressure.

In warm climates (*e.g.*, the South of France) sea water is evaporated by the heat of the sun in large flat ponds, called **salt meadows** (Fig. 203); the salt so made is called **solar salt**.



FIG. 203. —A SALT WORKS.  
From *De Re Metallica*, 1556.

The mother-liquor, called **bittern**, contains the magnesium salts and bromides (p. 330) of the sea water. This process was formerly carried on near Portsmouth, and at Lymington.

**The industrial uses of common salt.**—Besides its use in flavouring food and assisting digestion, common salt finds a large number of applications in industry. Very large quantities of salt are used in the **alkali industry**, for producing sodium carbonate and caustic soda, and salt is also largely used in preserving fish and other foods. Salt is used in glazing common earthenware, such as drain pipes. It is used in melting snow and ice on roads, an effect due to the lowering of the freezing point of water by the dissolved salt (p. 174).

**The history of chlorine.**—In 1648 Glauber obtained a strongly acid spirit of salt by heating moist salt in a charcoal furnace (Fig. 204) and condensing the fumes in receivers. A mixture of salt, alum, and copperas (ferrous sulphate) heated in the furnace gave a better yield. In 1658 he obtained spirit of salt by distilling common salt with concentrated sulphuric acid and condensing the fumes in water. The other product of the reaction was sodium sulphate, called **Glauber's salt**,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . In 1772 Priestley found that the product of the action of sulphuric



acid on salt was a permanent gas, which could be collected over mercury, but was very soluble in water. The solution of the



FIG. 203.—SALT MEADOWS.

gas was spirit of salt, which was then called the *marine acid*, or *muriatic acid* (from Latin *muria* = brine). Lavoisier (1789) regarded it as the oxide of an unknown element.

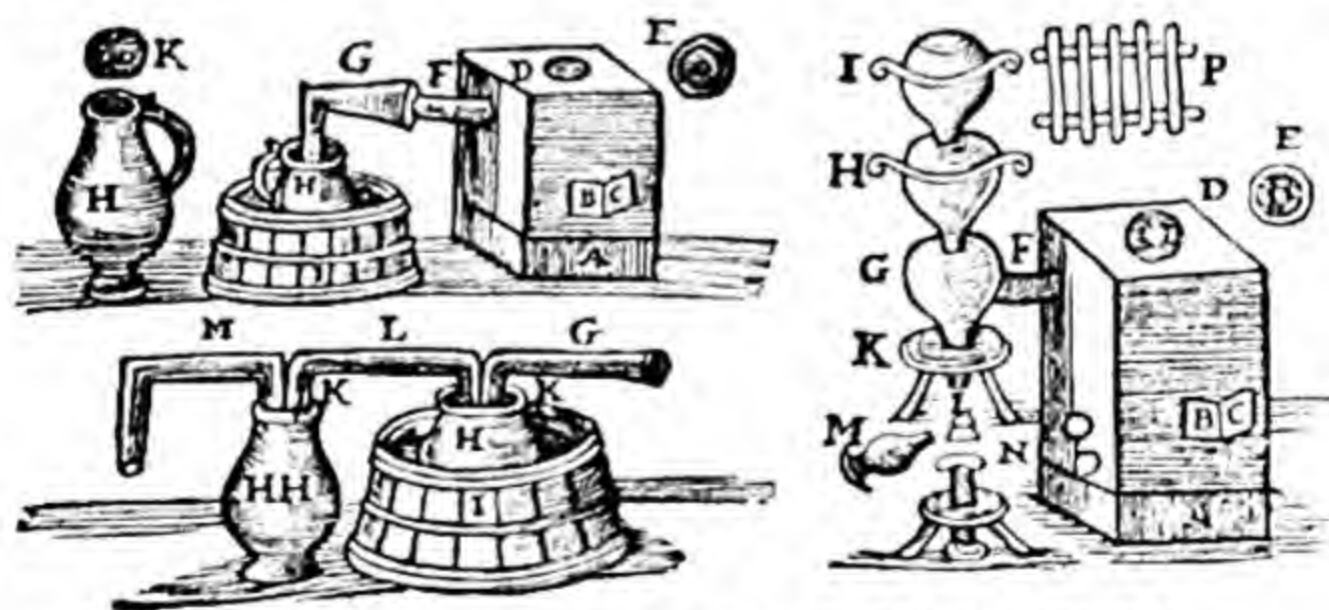


FIG. 204.—APPARATUS USED BY GLAUBER.

ON THE RIGHT IS A FURNACE FOR DISTILLATION, WITH RECEIVERS G, H, I. ON THE LEFT IS A RECEIVER COOLED IN A TUB OF WATER, AND BELOW IS SHOWN THE METHOD OF CONNECTING TWO RECEIVERS TOGETHER.

(From Glauber's *Philosophical Furnaces*, 1652.)

In 1774 Scheele examined the action of muriatic acid on black oxide of manganese, or manganese dioxide. He found that this dissolved in the cold acid with the production of a dark brown solution, which on warming gave off a greenish-yellow gas, which had a powerful odour and bleached vegetable colours. Scheele regarded this gas as muriatic acid deprived of its phlogiston by the manganese, and since he considered hydrogen

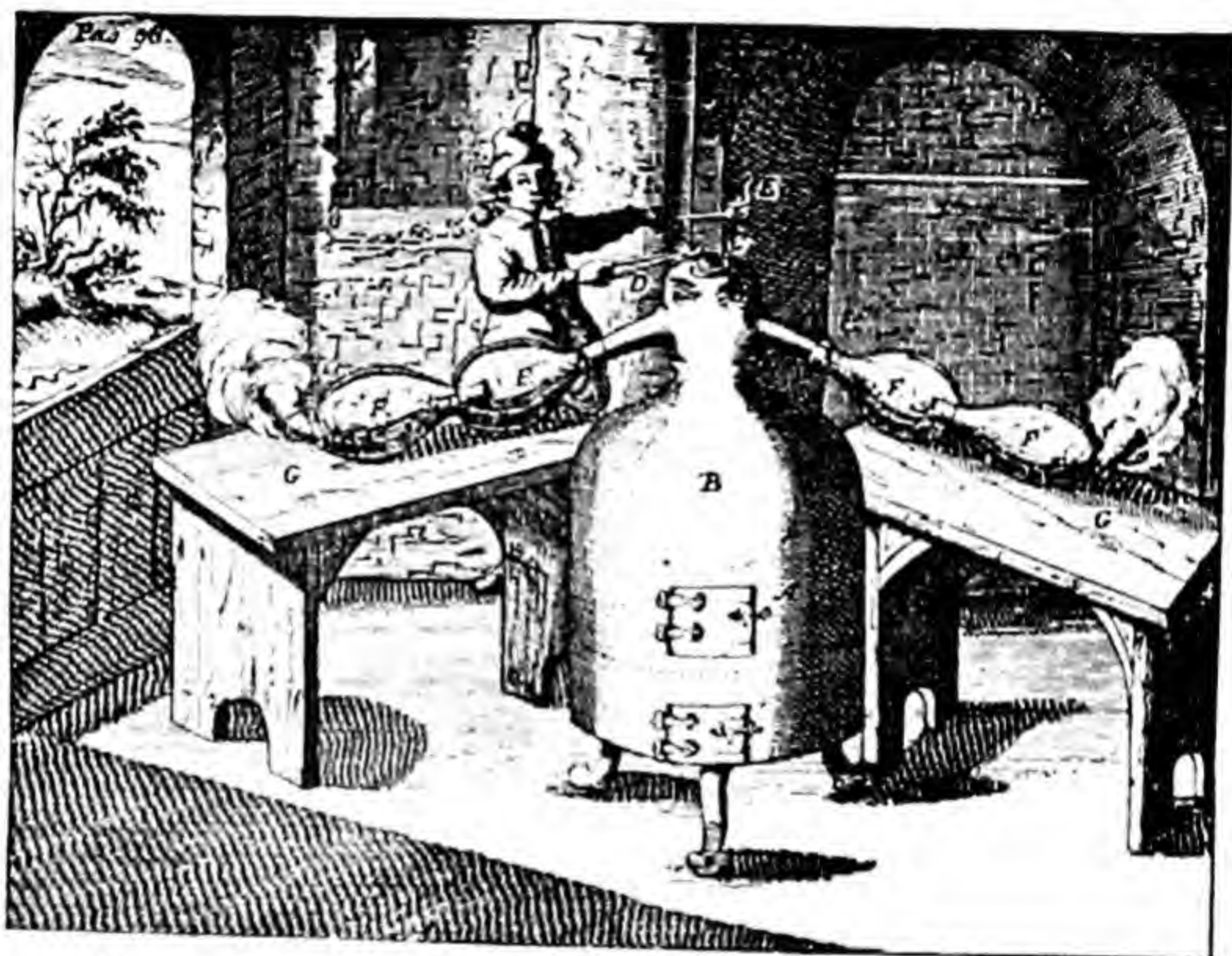


FIG. 205.—DISTILLATION APPARATUS USED BY GLAUBER.

to be phlogiston, this amounts to the same thing as muriatic acid deprived of hydrogen: Muriatic acid - Hydrogen. This we now know to be correct.

In 1785 Berthollet found that when a solution of the new gas in water was exposed to light, it gave off bubbles of oxygen and left a solution of muriatic acid. In accordance with Lavoisier's theory, he considered that the gas was a compound of muriatic acid and oxygen, or oxy-muriatic acid.

Gay-Lussac and Thenard in 1809 heated sodium in muriatic acid gas, and found that hydrogen was evolved and common salt remained. They were unable to obtain oxygen from the latter or to oxidise charcoal heated to whiteness in the gas. Nevertheless, they decided in favour of Lavoisier's view, and



rejected the alternative that the gas was a compound of 'oxy-muriatic acid,' which was really an element, and hydrogen.

The elementary nature of oxy-muriatic acid was, however, strongly urged by Davy in 1810. He heated charcoal, sulphur,

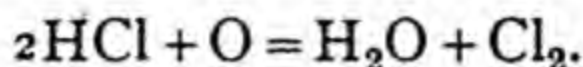


FIG. 206.—SIR HUMPHRY DAVY, 1778-1829.

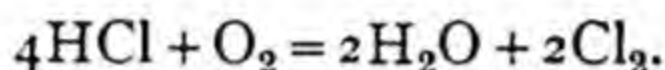
and metals in the gas, but never obtained any known oxygen compound. He proposed to regard it as an element, and called it **chlorine** (Greek *chloros* = pale green). In Berthollet's experiment, the oxygen came from the water, the hydrogen of which united with the chlorine to form muriatic, or hydrochloric, acid:  $\text{H}_2\text{O} + \text{Cl}_2 = 2\text{HCl} + \text{O}$ . Dry chlorine, Davy found, did not bleach.

## CHLORINE

**The preparation of chlorine.**—Chlorine is usually prepared in the laboratory by the oxidation of hydrochloric acid by free or combined oxygen :



*Free* oxygen will oxidise hydrochloric acid gas at a dull red heat in presence of a catalyst, *e.g.*, when a mixture of air and hydrochloric acid gas is passed over heated pumice containing a copper salt :



A stream of air is passed through concentrated sulphuric acid in a Woulfe's bottle, and concentrated hydrochloric acid allowed to drop slowly into the latter. The mixture of air and hydrochloric acid gas is passed through a hard glass tube packed with pieces of pumice which have been soaked in a solution of copper chloride and dried, and the tube is heated in a furnace (Fig. 207)

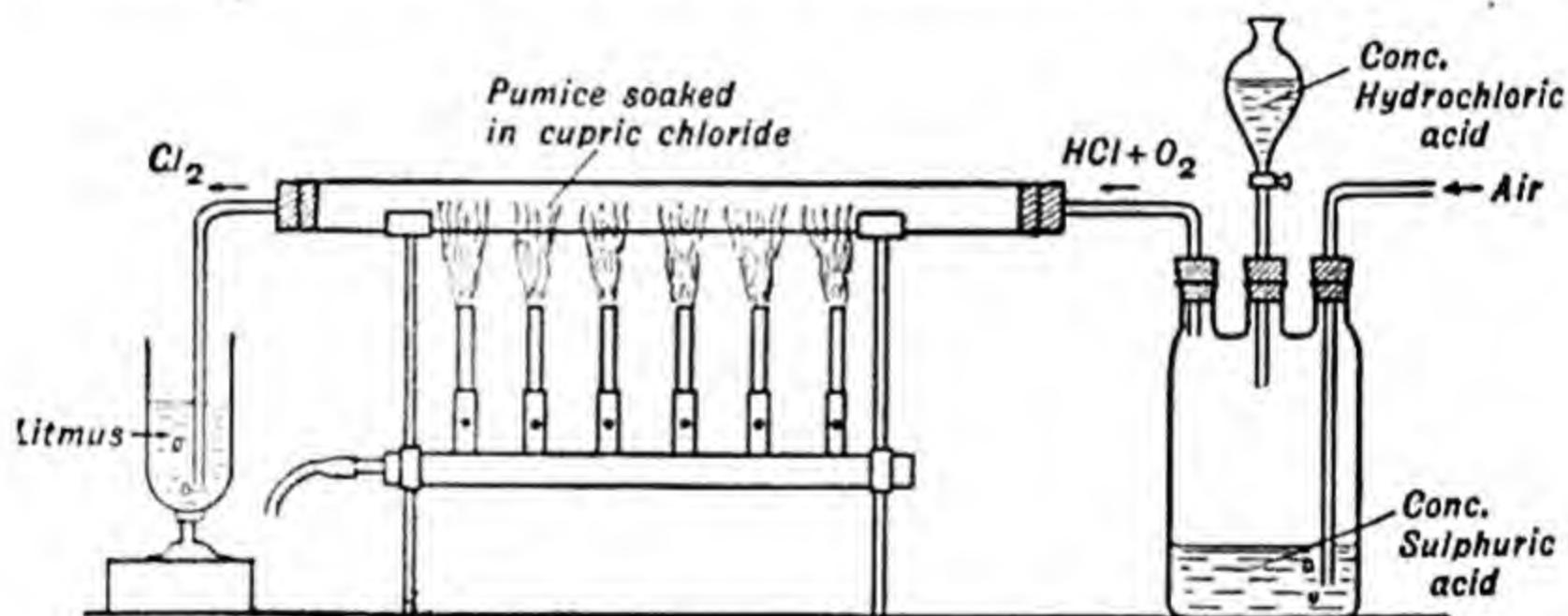


FIG. 207.—OXIDATION OF HYDROGEN CHLORIDE BY MEANS OF ATMOSPHERIC OXYGEN IN PRESENCE OF A CATALYST. PRINCIPLE OF THE DEACON PROCESS.

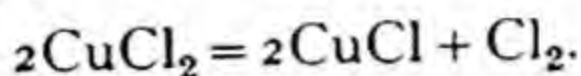
to a dull red heat. The gas may be passed through litmus solution, which is rapidly bleached by the chlorine evolved.

This reaction was used on the large scale for the production of chlorine by **Deacon's process**. It is not a convenient laboratory method, since the chlorine obtained is largely diluted with atmospheric nitrogen.

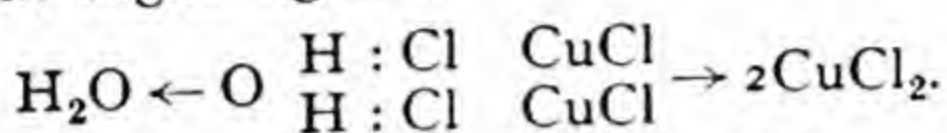
The catalytic action of the copper salt is explained as follows.



The cupric chloride decomposes on heating to form cuprous chloride and chlorine :



In presence of oxygen and cuprous chloride the hydrogen chloride is decomposed to form water and cupric chloride, and the reaction then begins again :



Copper sulphate if used as a catalyst is first converted into the chloride.

Hydrochloric acid may also be oxidised by *combined* oxygen. The common *laboratory* method for the preparation of chlorine is to heat a mixture of manganese dioxide and concentrated hydrochloric acid in a flask (Fig. 208). The reaction probably takes

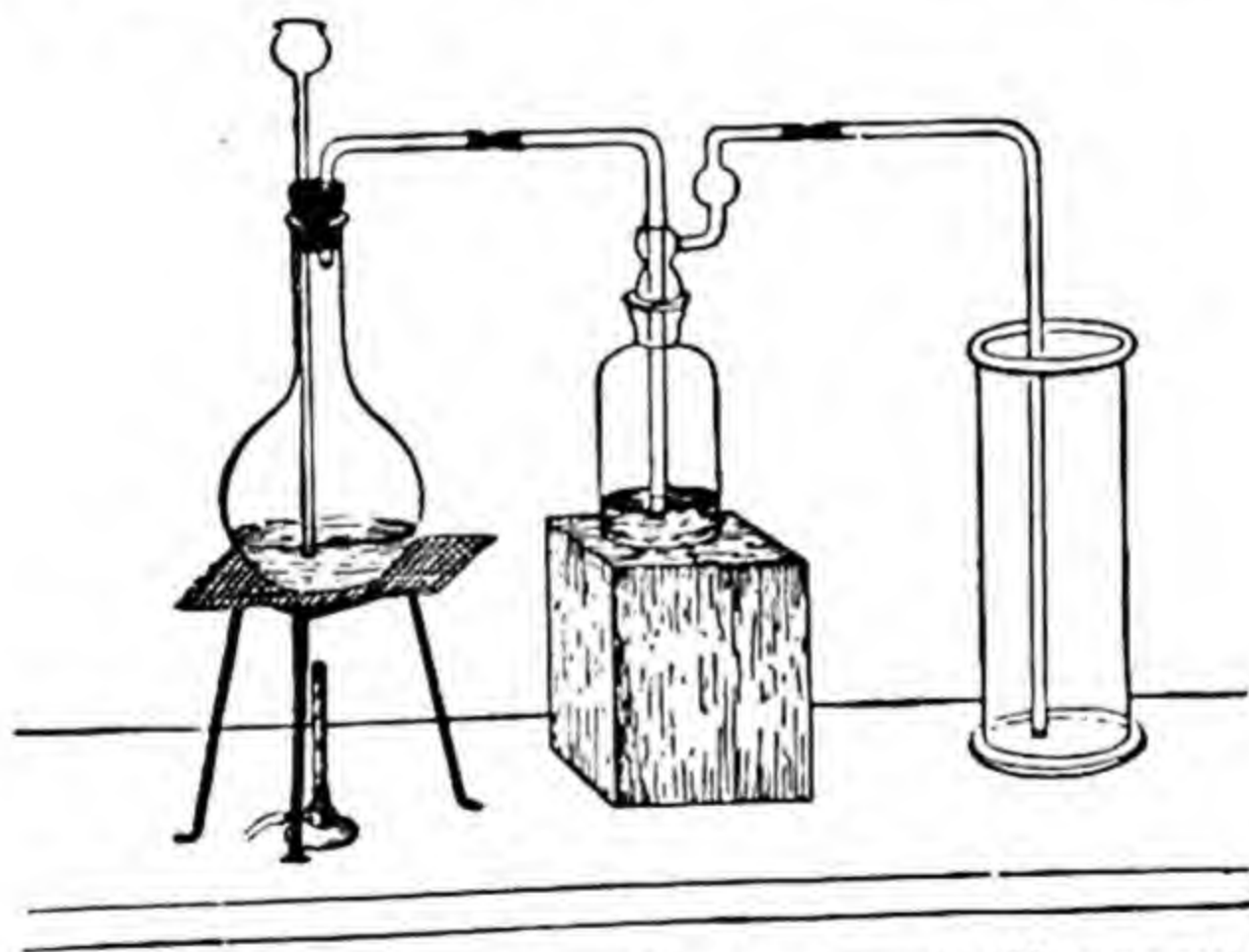
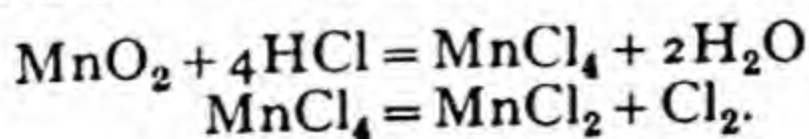
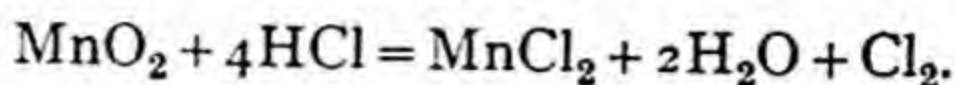


FIG. 208.—PREPARATION OF CHLORINE FROM HYDROCHLORIC ACID AND MANGANESE DIOXIDE.

place in two stages, a higher chloride of manganese,  $\text{MnCl}_4$  or  $\text{MnCl}_3$ , is first formed in the cold as a dark brown solution, which decomposes on heating with the evolution of chlorine and the formation of colourless or faintly pink manganous chloride,  $\text{MnCl}_2$  :



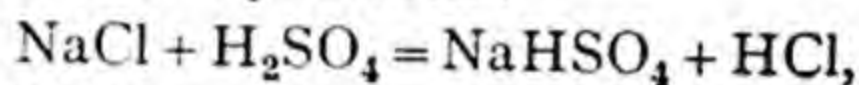
The complete reaction is therefore :



The gas is washed with a little water in a wash bottle to free it from hydrochloric acid and is then collected in dry jars by downward displacement, since it is more than twice as heavy as air. The residue in the flask is usually yellow, due to ferric chloride formed from iron oxide in the commercial manganese dioxide.

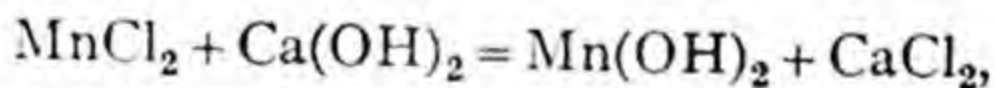
Chlorine has a powerful action on the mucous membranes and the experiment must be performed in a fume cupboard. The gas may also be collected over a saturated solution of common salt, but it is too soluble in water to be collected over that liquid, and it attacks mercury. Chlorine may be dried by means of calcium chloride or concentrated sulphuric acid.

Instead of hydrochloric acid, a mixture of common salt and sulphuric acid may be heated with manganese dioxide, when hydrochloric acid is first produced :

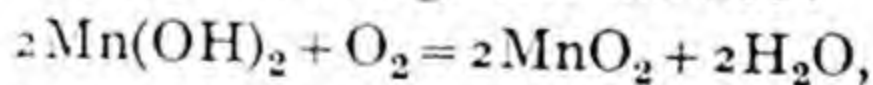


and is then oxidised by the manganese dioxide.

Chlorine was formerly obtained on the technical scale from manganese dioxide and the hydrochloric acid obtained in the Leblanc process (*q.v.*) by heating them together by means of steam in stone stills. To recover the manganese from the still liquor, Weldon's process was used. An *excess* of milk of lime was added to the liquor, so as to precipitate manganous hydroxide :

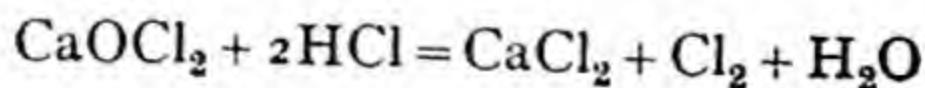


and leave free calcium hydroxide in suspension. Air was then blown through, and *in presence of free lime*, the manganous hydroxide was oxidised to manganese dioxide :



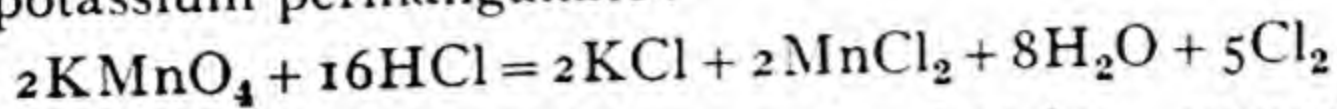
which is a weakly acidic oxide and combines with the lime to form what is called *Weldon mud*,  $\text{CaO} \cdot 2\text{MnO}_2$ . This was decomposed by hydrochloric acid to give chlorine, and the still liquor worked up again, and so on. The Weldon process is now very little used.

Chlorine may be prepared conveniently in small quantities by the action of cold concentrated hydrochloric acid on bleaching powder :

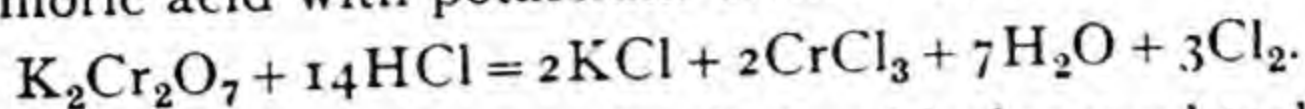




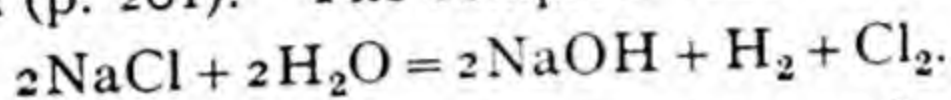
or on potassium permanganate :



(which gives *pure* chlorine), or by heating concentrated hydrochloric acid with potassium dichromate :



**Electrolytic chlorine.**—Nearly all the chlorine used technically is obtained by the electrolysis of a solution of common salt. Chlorine is deposited at the anode, and the sodium ions deposited on the cathode react with the water to form caustic soda and hydrogen (p. 201). The complete reaction is :



The caustic soda is an important product, and the chlorine is often obtained as a by-product.

Various types of electrolytic cell are used, the main object being to prevent the chlorine evolved at the anode from coming in contact with the caustic soda formed at the cathode, when reaction would occur between them (p. 323).

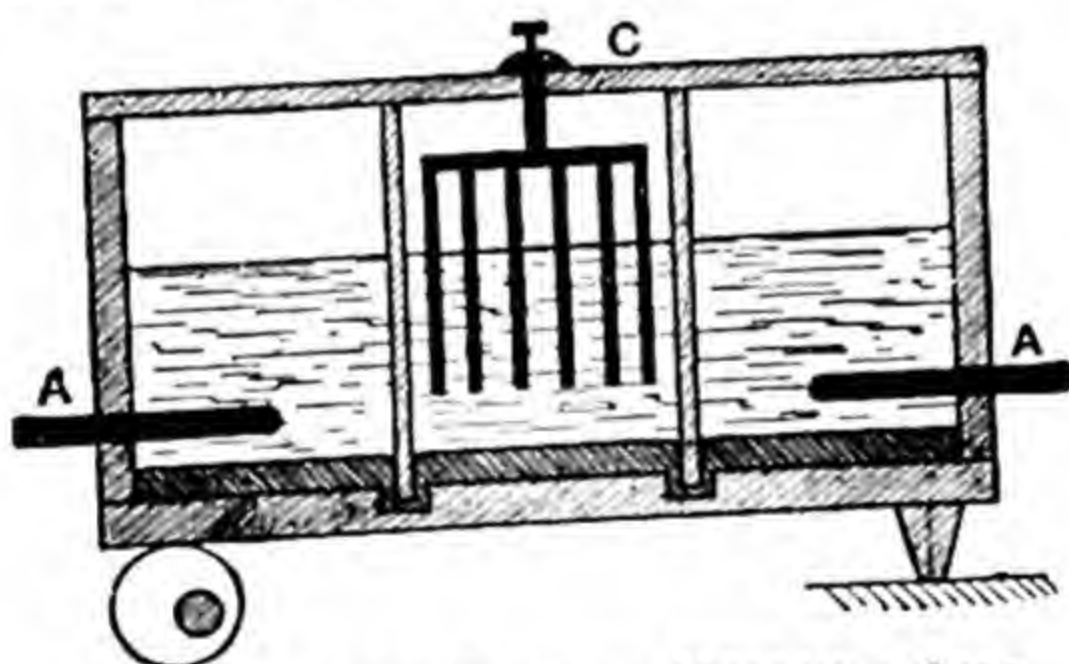


FIG. 209.—THE CASTNER-KELLNER CELL.

The **Castner-Kellner** cell consists (Fig. 209) of a shallow slate tank divided into three compartments by slate partitions not quite touching the floor. The floor is covered by a pool of mercury, thus separating the three compartments. Each end compartment is filled with strong brine, the middle one with water. Anodes of carbon are placed in the end compartments, whilst the cathode consists of a bundle of iron rods in the central compartment. Chlorine is evolved in the end compartments, and is led off by earthenware pipes. Sodium is discharged on the mercury in the end compartments, and dissolves to form

sodium amalgam. The cell is given a slow rocking motion by an eccentric, and the amalgam is brought from the end compartments to the middle compartment, where it decomposes the water, forming a solution of caustic soda. Hydrogen is evolved from the iron cathode.

In the Gibbs cell (Fig. 210), used by the United Alkali Co., the anodes are carbon rods and are separated from the cylindrical

iron cathode by a diaphragm of asbestos paper. The solution of caustic soda then obtained is not so pure as that obtained in the Castner-Kellner cell, and the sodium chloride contained in it must be separated.

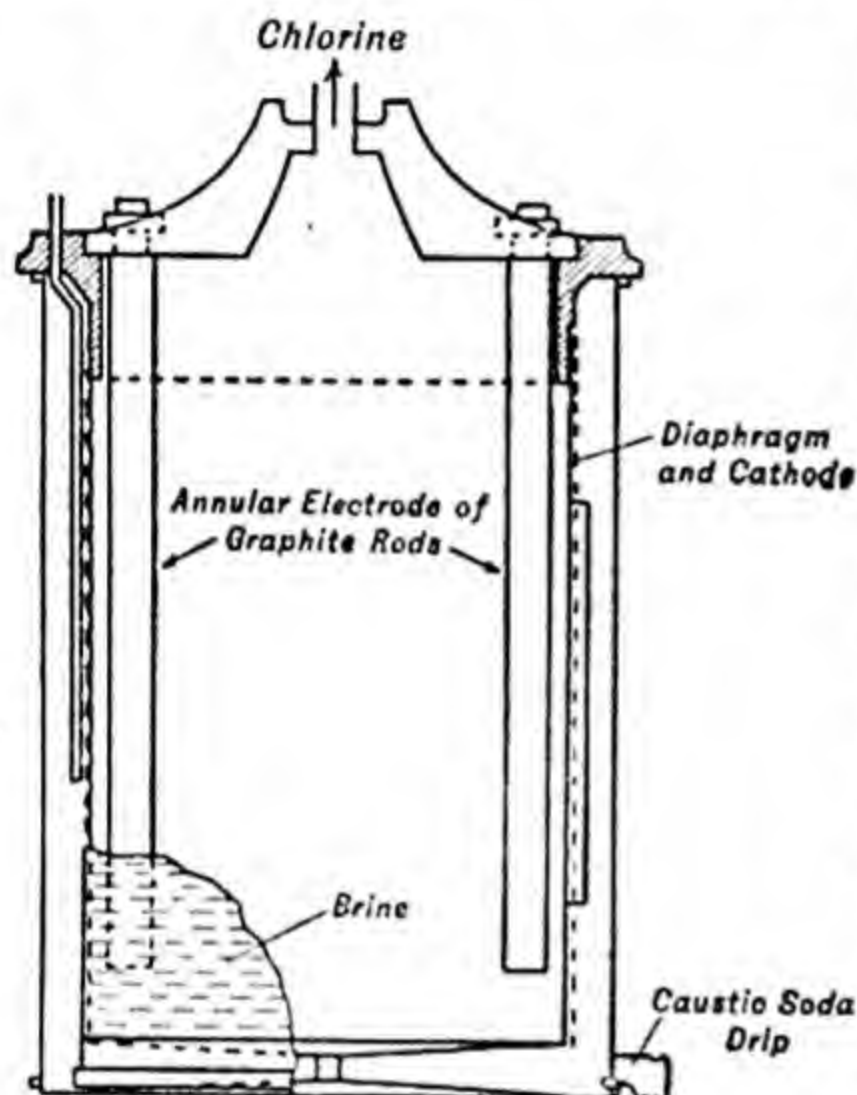


FIG. 210.—THE GIBBS CELL.

Most of the chlorine is used for bleaching, and in refining petroleum, either as such or (usually) as *hypochlorites* (*q.v.*) of sodium or calcium, the latter in the form of *bleaching powder*. By causing the hydrogen and chlorine gases from the electrolytic cell to unite, **synthetic hydrochloric acid** may be produced.

Electrolytic chlorine is fairly easily liquefied by cooling and

compression. The liquid is transported in gas-tight cylinders or tank wagons of iron, since this metal is not attacked by *dry* chlorine. Liquid chlorine has an orange yellow colour: in liquid air it freezes to a pale yellow solid.

**Properties of chlorine.**—Chlorine is a greenish-yellow gas with a most irritating odour and a violently corrosive action on the mucous membranes. It is fairly soluble in water, and since it is heavier than air it is collected by downward displacement. It can be dried by concentrated sulphuric acid or calcium chloride.

Chlorine is a *very active element*; it combines readily with hydrogen, and directly with most metals, and non-metallic elements except nitrogen, oxygen, and carbon. Combination may occur when the elements are brought together at the ordinary temperature, often with the production of flame, or incandescence.



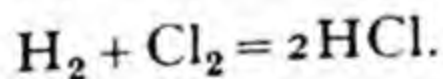
The reactions with metals, which occur violently with moist gas, do not always take place if the chlorine is *dry*, although pure dry mercury completely absorbs pure dry chlorine.

A little finely powdered arsenic or antimony sprinkled into a jar of chlorine burns, producing *poisonous* fumes of the chlorides  $\text{AsCl}_3$  and  $\text{SbCl}_5$ , respectively.

A piece of phosphorus in a deflagrating spoon ignites spontaneously in chlorine, burning with a pale flame, and producing fumes of the chlorides  $\text{PCl}_3$  and  $\text{PCl}_5$ .

When chlorine is passed over sodium heated in a hard glass bulb tube (Fig. 211), the metal catches fire and burns with an exceedingly brilliant yellow flame, producing white sodium chloride,  $\text{NaCl}$ .

A jet of hydrogen burning in air continues to burn, with an enlarged greenish flame, when introduced into a jar of chlorine (Fig. 186), and the hydrogen chloride formed produces fumes in moist air :



A mixture of equal volumes of hydrogen and chlorine explodes violently when ignited by a taper, or when the mixture in a thin glass bulb is exposed to bright sunlight or to the light of burning magnesium. Combination occurs slowly when the mixture is exposed to diffused daylight but the gases do not react in the dark.

Chlorine has a great *affinity for hydrogen* and will remove it from many compounds. Chlorine, for example, will remove hydrogen from water, setting free the oxygen :

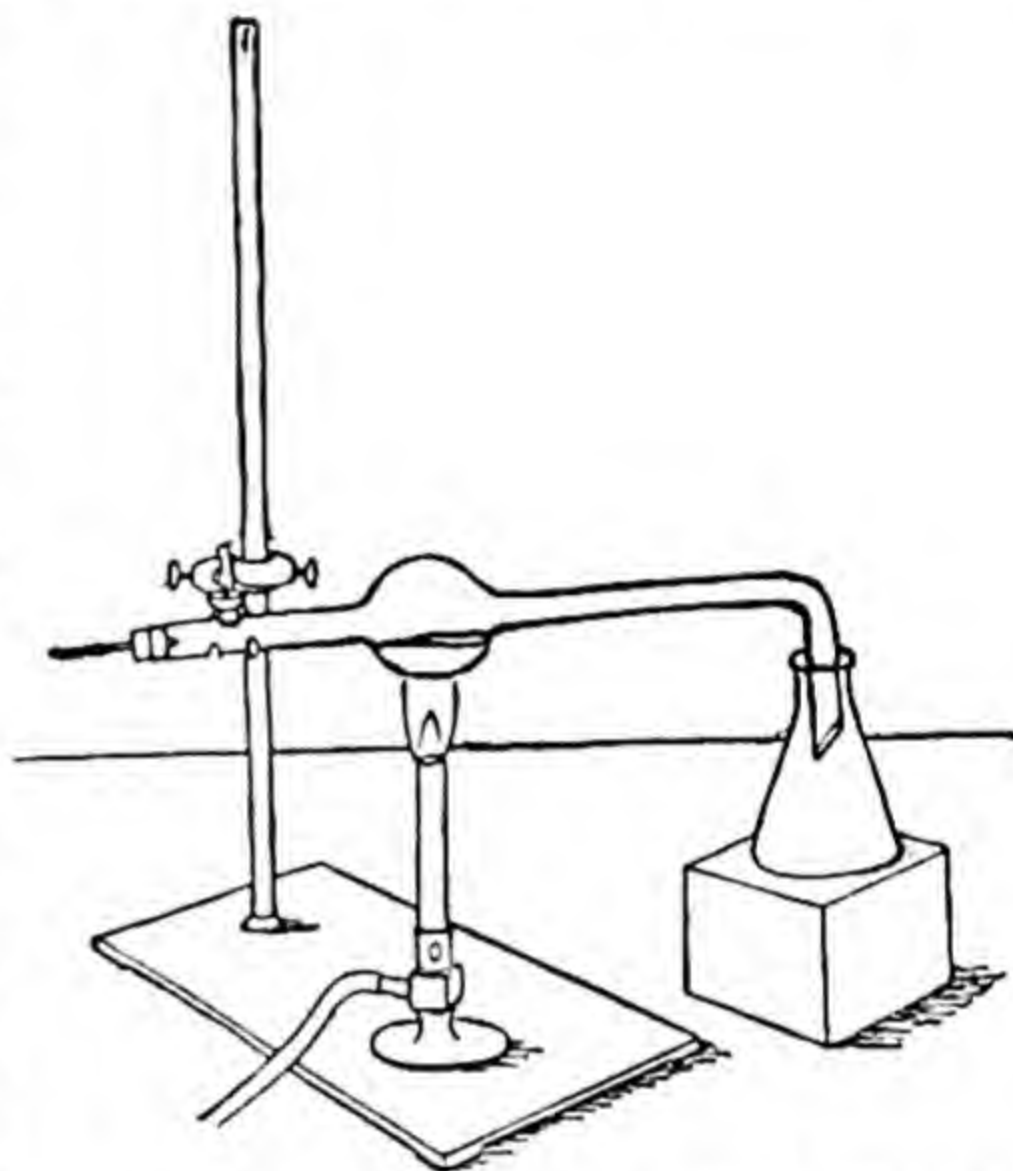
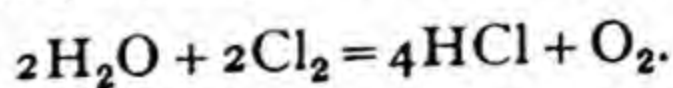


FIG. 211.—BURNING SODIUM IN CHLORINE.

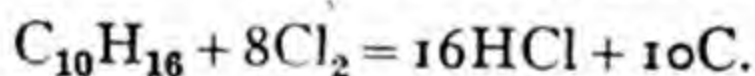
This reaction, which is the reverse of Deacon's process (p. 312), takes place when steam and chlorine are passed through a heated tube (p. 278), or even when **chlorine water** (a solution of chlorine in water) is exposed to sunlight in an inverted flask, when bubbles of oxygen are evolved and a solution of hydrochloric acid remains. Chlorine also removes hydrogen from compounds of carbon and hydrogen, setting free the carbon.

A burning taper plunged into a jar of chlorine burns with a small dull-red flame, clouds of black carbon and white fumes of hydrochloric acid being evolved. Wax is a mixture of *hydrocarbons*, or compounds of carbon and hydrogen. The chlorine removes the hydrogen, forming hydrogen chloride, and sets free the carbon, with which it does not combine directly.

A mixture of 2 vols. of chlorine and 1 vol. of ethylene,  $C_2H_4$ , when ignited, burns with a red flame, emitting dense black clouds of carbon :  $C_2H_4 + 2Cl_2 = 2C + 4HCl$ .

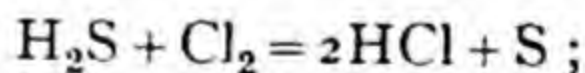
A mixture of 2 vols. of chlorine and 1 vol. of methane,  $CH_4$ , ignited with a taper, burns, giving fumes of hydrochloric acid and a cloud of carbon :  $CH_4 + 2Cl_2 = C + 4HCl$ .

A little turpentine,  $C_{10}H_{16}$ , heated in a test-tube and poured on filter-paper, catches fire when plunged into chlorine, giving a black cloud of carbon and fumes of hydrochloric acid :

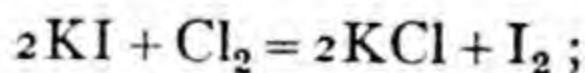


Chlorine combines with sulphur dioxide,  $SO_2$ , carbon monoxide,  $CO$ , and ethylene,  $C_2H_4$ , producing sulphuryl chloride,  $SO_2Cl_2$ , carbonyl chloride (*phosgene*),  $COCl_2$ , and ethylene dichloride,  $C_2H_4Cl_2$ , respectively.

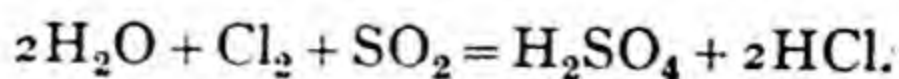
A solution of chlorine in water (chlorine water), which has a pale greenish-yellow colour and smells strongly of the gas, possesses strong bleaching and oxidising properties. It precipitates sulphur from a solution of sulphuretted hydrogen :



it liberates iodine from a solution of potassium iodide :



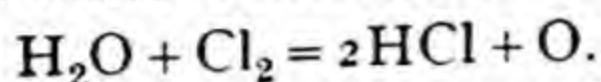
and a solution of sulphur dioxide (sulphurous acid) is oxidised to sulphuric acid :



On exposure to light it is decomposed (see above).



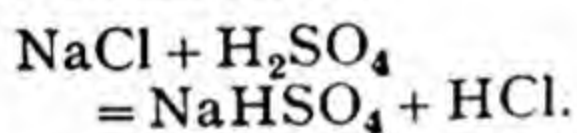
**Bleaching by chlorine.**—Chlorine is used in large quantities for *bleaching*. The colouring matter is *oxidised* by *nascent* oxygen set free from water which must also be present :



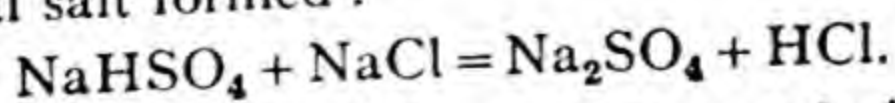
*Dry* chlorine does not bleach : a piece of red flannel remains unchanged in a jar of dry chlorine, but if a little water is introduced the colour is rapidly bleached. The disinfecting action of chlorine is also due to oxidation (*cf.*  $\text{H}_2\text{O}_2$ , p. 304).

### HYDROGEN CHLORIDE OR HYDROCHLORIC ACID.

**Hydrogen chloride, or hydrochloric acid.**—Chlorine and hydrogen form only one compound, hydrogen chloride, or hydrochloric acid,  $\text{HCl}$ . This is formed by the combustion of hydrogen in chlorine, but is usually prepared by the action of concentrated sulphuric acid on common salt :



One only of the two hydrogen atoms of sulphuric acid is expelled, and the acid salt,  $\text{NaHSO}_4$ , sodium hydrogen sulphate, or sodium bisulphate, is formed, unless the temperature is higher than can conveniently be attained in a glass flask. This salt, which contains one of the hydrogen atoms of the sulphuric acid, has a strongly acid reaction and if *strongly* heated with common salt, the remaining hydrogen atom is displaced as hydrochloric acid, and the normal salt formed :



In the *laboratory preparation* common salt is placed in a

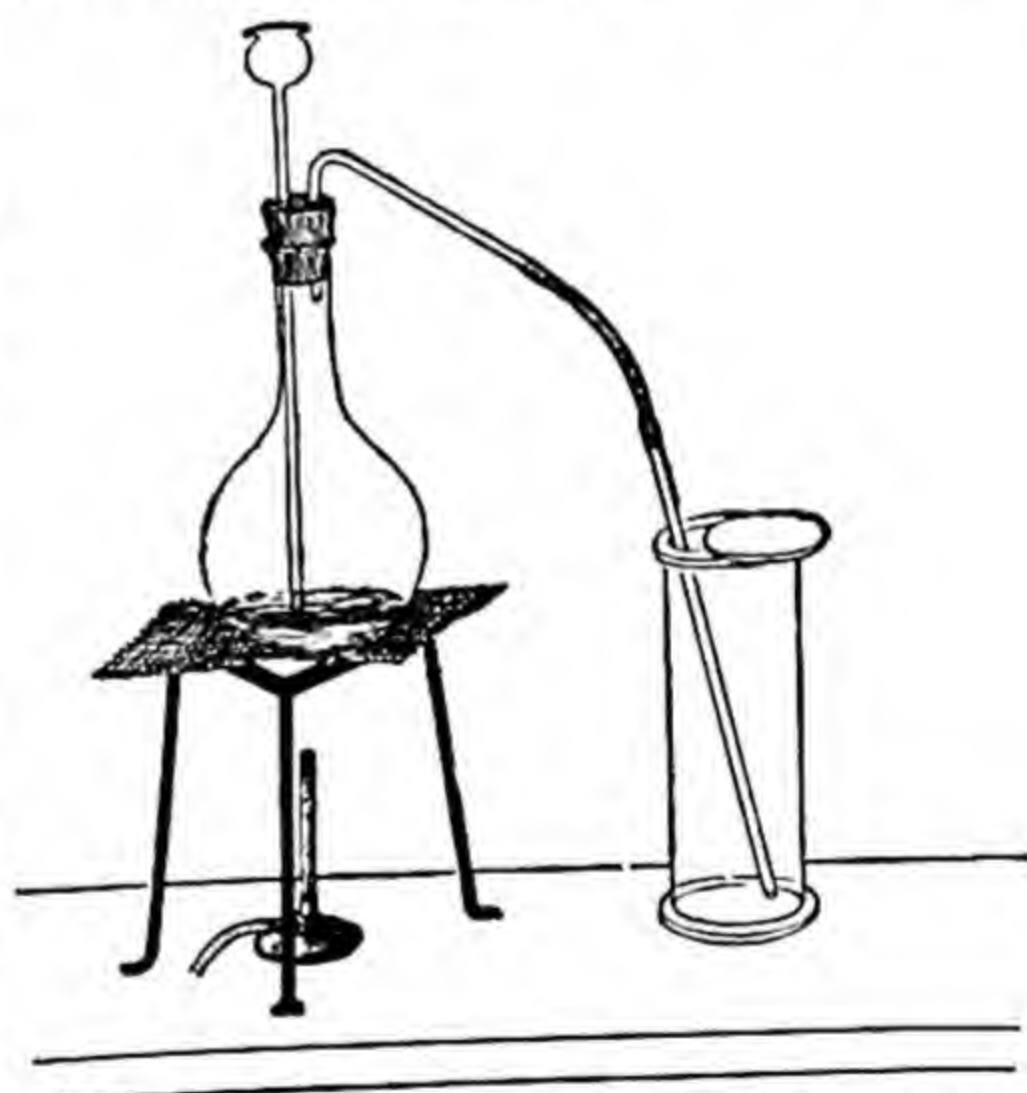
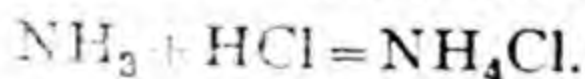


FIG. 212.—PREPARATION OF HYDROGEN CHLORIDE GAS FROM COMMON SALT AND CONCENTRATED SULPHURIC ACID.

fairly large flask (so as to allow space for frothing) and concentrated sulphuric acid added through a thistle funnel (Fig. 212). Some gas is evolved at once, but when the reaction slackens the flask is gently heated over wire gauze. The gas is collected in dry jars by downward displacement, as it is slightly heavier than air. When the jar is filled with gas, copious white fumes issue from the mouth. These are formed by the action of atmospheric moisture on the gas, producing a mist of small droplets of concentrated hydrochloric acid: the dry gas is quite transparent and does not fume with *dry* air. The gas may be dried by concentrated sulphuric acid or calcium chloride and collected over mercury.

On the technical scale the reaction is carried out in a special gas-tight furnace called a *salt cake furnace* containing an iron pan for the first stage of the process leading to the formation of  $\text{NaHSO}_4$ , and a hearth or fireclay box (*muffle*) in which the pasty mass from the pan is more strongly heated to complete the reaction with formation of  $\text{Na}_2\text{SO}_4$  (*salt cake*). The gas is absorbed by water trickling over coke in a large brickwork or stone tower to form a crude solution of hydrochloric acid, called *spirit of salt*, or *muriatic acid*, which is yellow on account of impurities (*e.g.*, iron salts). This acid is transported in large globular glass bottles called *carboys*, packed with straw into iron crates, or in large stoppered bottles called *Winchester quarts*. Some hydrochloric acid is made from hydrogen and chlorine (p. 316). The acid is used for cleaning metals and other purposes.

**Properties of hydrogen chloride.**—Hydrogen chloride, or hydrochloric acid gas, is a colourless gas with a very pungent irritating odour, and attacks the mucous membranes of the nose and throat. It is not combustible and is a non-supporter of combustion. It is liquefied with difficulty. The gas, and its concentrated solution, fume in moist air, and form dense white fumes of ammonium chloride when brought in contact with ammonia gas:



The gas is very soluble in water, forming a very acid solution.

The great solubility of hydrochloric acid gas in water may be demonstrated by the fountain experiment. A large, dry, round-bottomed flask is filled with the gas and fitted with a rubber stopper carrying inside the flask a tube drawn out into a jet. The flask is inverted with the tube dipping into water coloured with blue litmus contained in a second large flask, as



shown in Fig. 213. By blowing into the short tube on the second flask a drop of water is forced into the upper flask. The gas is instantly dissolved, the water in the lower flask is driven in the form of a fountain into the upper flask, and the litmus is turned red by the acid solution formed.

When a *dilute* solution of hydrochloric acid is distilled, a weak acid first passes over, and the residue in the retort increases in concentration, with rise of boiling point. When the concentration reaches 20.2 per cent., the liquid then distils over unchanged with a constant composition and boiling point of  $110^{\circ}$ . This is called the **constant boiling solution**. If *concentrated* hydrochloric acid is distilled, it first loses hydrogen chloride gas, with a little moisture, till the residue again attains the composition of 20.2 per cent. and distils over at  $110^{\circ}$ , this being the *maximum boiling point* of

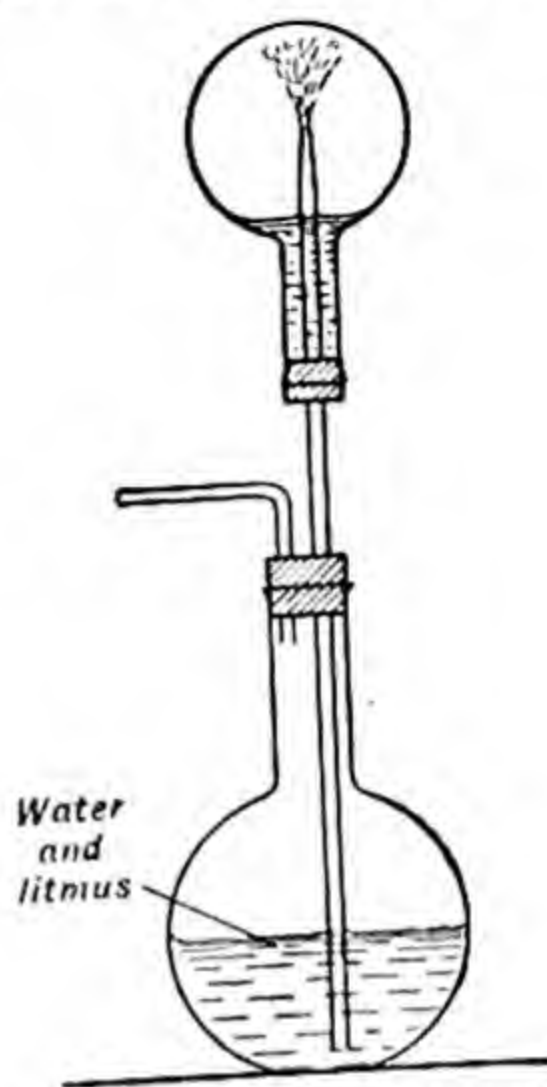


FIG. 213.—THE 'FOUNTAIN EXPERIMENT' FOR DEMONSTRATING THE SOLUBILITY OF A GAS.

the acid. The constant boiling solution varies in composition with the pressure; hence it is not a true chemical compound.

**Composition of hydrogen chloride.**—The composition of hydrogen chloride may be determined either by *analysis* or by *synthesis*. Two examples of each method will be described.

**Analytical methods.**—The first method is the electrolysis of hydrochloric acid of specific gravity 1.1 with gas carbon electrodes in the apparatus shown in Fig. 214. Gas carbon is used instead of platinum for the electrodes, since platinum is attacked by chlorine. After the liquid has become saturated with chlorine, hydrogen and chlorine are evolved in equal volumes.

The second method is to decompose dry

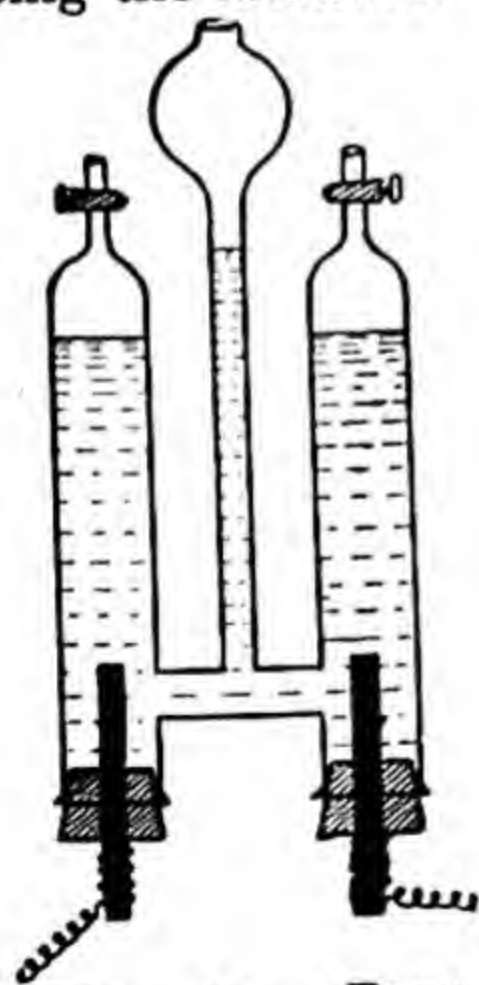


FIG. 214.—ELECTROLYSIS OF HYDROCHLORIC ACID.

hydrogen chloride gas by means of liquid sodium amalgam in the apparatus shown in Fig. 215. After standing for a day, a white crust of sodium chloride is formed and, after adjusting the

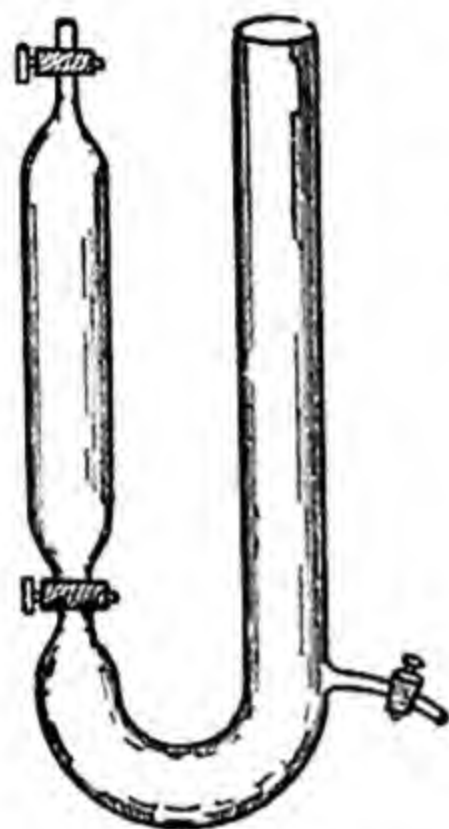


FIG. 215.—DECOMPOSITION OF HYDROGEN CHLORIDE GAS BY SODIUM AMALGAM.

levels by pouring mercury into the open limb, it will be seen that half the original volume of gas is left. This may be displaced through the upper stopcock and shown, by applying a lighted taper to it, to be hydrogen.

*Synthetic methods.*—In the first method one half of the glass tube provided with three stopcocks, shown in Fig. 216, is filled with chlorine and the other half with hydrogen. The middle stopcock is now opened and the gases allowed to mix. This must be done in a room with diffused daylight, for in *sunlight* the gases combine with explosion. After a few hours, combination is complete and the greenish colour of the chlorine has disappeared. When one of the end stopcocks is opened

under mercury, it is seen that there is no change in volume; if it is opened under water the latter dissolves the hydrogen chloride and fills the tube.

In the second method a mixture of equal volumes of hydrogen and chlorine is passed, in the dark, into the tube shown in Fig. 217, provided with platinum wires for exploding the gas by a spark. The tube is placed behind a strong glass screen and a spark passed. There is a flash of light in the tube and a click is heard. When the tube is cool it is opened



FIG. 216.—SYNTHESIS OF HYDROGEN CHLORIDE.

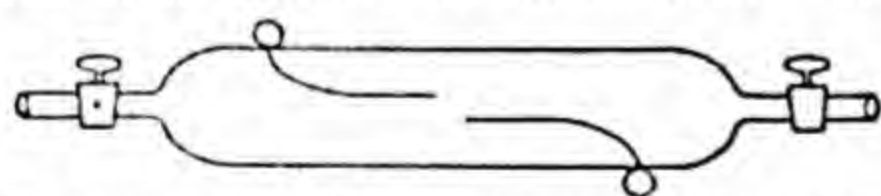


FIG. 217.—EXPLOSION OF A MIXTURE OF HYDROGEN AND CHLORINE.

under mercury and water successively, with similar results to those described above.

The experiments show that:

1 vol. hydrogen + 1 vol. chlorine = 2 vols. hydrogen chloride;  
 $\therefore$  1 mol. hydrogen + 1 mol. chlorine = 2 mols. hydrogen chloride,  
 since equal volumes contain equal numbers of molecules. Hence  
 1 molecule of hydrogen chloride contains half a molecule each



of hydrogen and chlorine. The formulae of the hydrogen and chlorine molecules are  $H_2$  and  $Cl_2$ , hence the molecule of hydrogen chloride contains one atom of hydrogen and one atom of chlorine, or the formula is  $HCl$ .

A solution of hydrochloric acid or a chloride gives with silver nitrate solution a white curdy precipitate of silver chloride,  $AgCl$ , insoluble in dilute nitric acid but easily soluble in ammonia.

**Compounds of chlorine with oxygen.**—Compounds of chlorine with oxygen are present in substances used in everyday life: *bleaching powder* or *chloride of lime*, *sodium hypochlorite*, and *potassium chlorate* ('chlorate of potash').

Chlorine forms two important oxides :

chlorine monoxide,  $Cl_2O$

chlorine dioxide,  $ClO_2$

and three important oxy-acids :

hypochlorous acid,  $HOCl$ ,

forming hypochlorites,

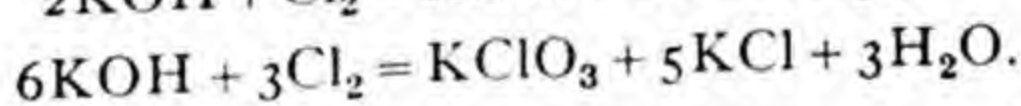
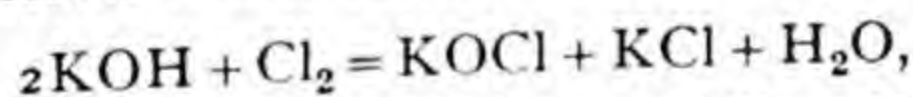
chloric acid,  $HClO_3$ ,

forming chlorates,

perchloric acid,  $HClO_4$ ,

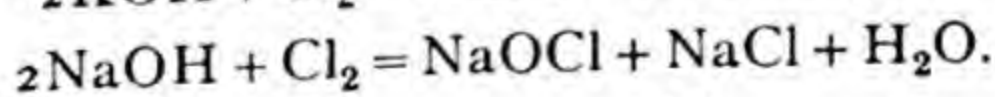
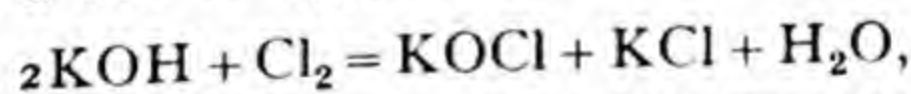
forming perchlorates.

Both hypochlorites and chlorates may be formed by the action of chlorine on caustic alkalies under different conditions, and in each case a chloride is also formed :



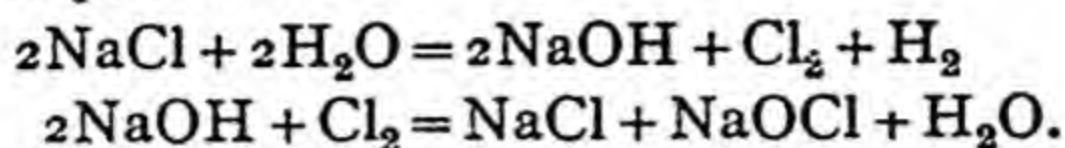
Hypochlorous acid, chloric acid, and most hypochlorites are known only in solution; perchloric acid, chlorates and perchlorates may be obtained in the pure state.

**Hypochlorites.**—When a stream of chlorine is passed into a cold solution of caustic potash or soda so that the alkali is always present in excess, it is absorbed, and a liquid with a peculiar odour, different from that of chlorine, is produced. This contains a salt of hypochlorous acid,  $HOCl$ , together with a chloride :

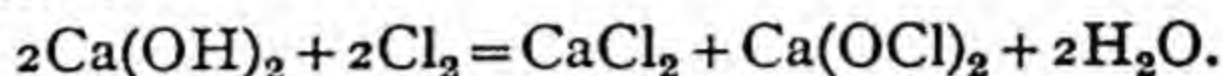


Sodium hypochlorite solution containing sodium chloride is used as a disinfectant and antiseptic ('Milton'; Dakin's solution): it may be prepared by the electrolysis of common salt solution so that the chlorine formed at the anode is allowed to

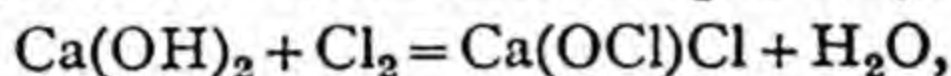
react with the sodium hydroxide formed at the cathode, and the liquid is kept cool :



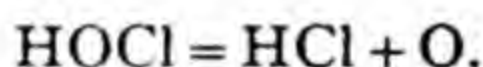
*Milk of lime* gives a solution of calcium chloride and calcium hypochlorite :



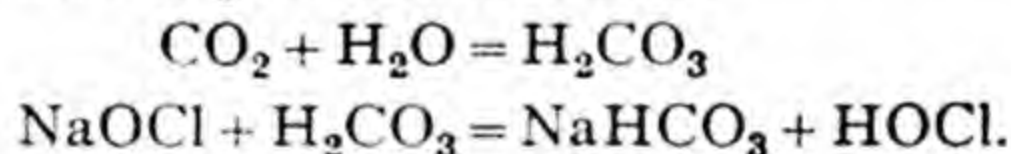
If instead of milk of lime, *dry slaked lime* is used, the product is **bleaching powder** (or 'chloride of lime'). This was regarded as a compound with the formula  $\text{CaOCl}_2$  or  $\text{Ca(OCl)Cl}$  :



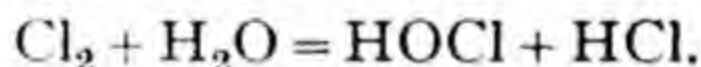
but its composition has more recently been given differently (p. 596). On solution in water it forms a solution containing calcium hypochlorite and calcium chloride. The bleaching action of hypochlorites and bleaching powder is due to the liberation of nascent oxygen from hypochlorous acid, which is unstable :



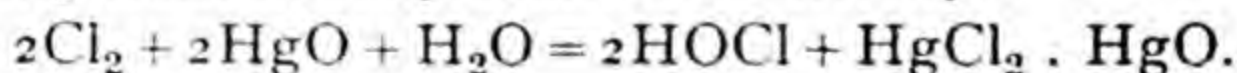
Hypochlorous acid is a very weak acid and is set free from its salts by atmospheric carbon dioxide, which forms the very weak carbonic acid in presence of water :



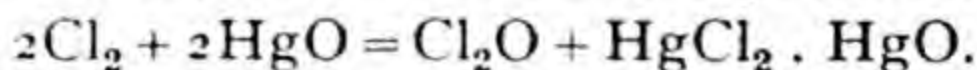
The bleaching action of chlorine water may be due to the hypochlorous acid which it contains :



A dilute solution of hypochlorous acid may be prepared by shaking chlorine water with yellow precipitated mercuric oxide, and filtering from the oxychloride of mercury :



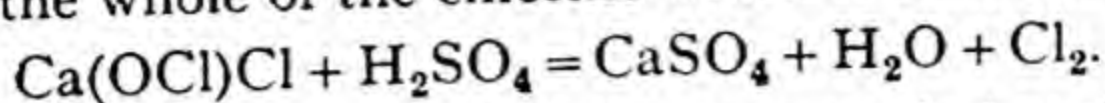
When chlorine is passed over *dry* mercuric oxide, the anhydride of hypochlorous acid, **chlorine monoxide**,  $\text{Cl}_2\text{O}$ , is formed :



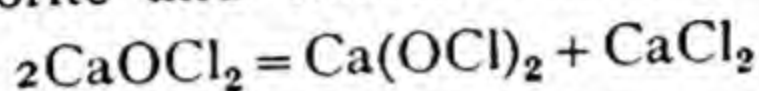
It is a yellow gas which condenses to a red liquid in a freezing mixture. Chlorine monoxide is explosive, decomposing into chlorine and oxygen. It dissolves in water to form hypochlorous acid.



The action of excess of a strong acid on bleaching powder is to liberate the whole of the chlorine which it contains :



Hence *all* the chlorine of bleaching powder is 'available,' *i.e.*, can be liberated as free chlorine by the action of strong acids. If a solution of bleaching powder is carefully treated with the calculated amount of dilute nitric acid, hypochlorous acid is formed and may be distilled off. The bleaching powder when dissolved in (or made into a paste with) water breaks down into calcium hypochlorite and calcium chloride :

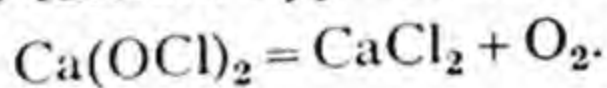


and the calcium hypochlorite is then decomposed by the dilute acid :

$$\text{Ca(OCl)}_2 + 2\text{HNO}_3 = \text{Ca(NO}_3)_2 + 2\text{HOCl}.$$

On account of the displacement of hypochlorous acid by atmospheric carbon dioxide, solutions of hypochlorites and also bleaching powder always smell of hypochlorous acid when exposed to air.

Bleaching powder readily gives off oxygen when it is made into a paste with water and warmed with a few drops of cobalt chloride solution. A black oxide of cobalt is precipitated (the bleaching powder contains a little free calcium hydroxide which precipitates cobalt oxide) which acts as a catalyst in the decomposition of the calcium hypochlorite in the solution :

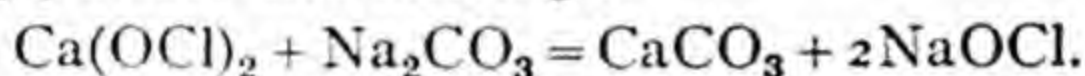


**\*Bleaching.**—Many colouring matters when oxidised yield colourless or feebly-coloured products. The yellow colour of unbleached cotton is due to natural brown colouring matters, which are removed by bleaching. The yarn or fabric is first singed by a flame or hot metal, then boiled with lime water, washed with dilute hydrochloric acid, and then boiled twice with a solution of soda-ash (sodium carbonate) followed by a solution of soda-ash, rosin and caustic soda. The material, from which a good deal of colour is now removed, is washed and immersed in bleaching powder solution, followed by immersion in dilute hydrochloric or sulphuric acid, which sets free the chlorine. After the bleaching action has occurred the material is washed, squeezed, and dried. The cellulose, of which the cotton fibres are composed, is resistant, unless the action is too prolonged, but the colour is oxidised. The remaining chlorine is removed by washing, and finally by treating with a substance such as

sodium thiosulphate, which reduces the chlorine and is an *antichlor* (p. 368).

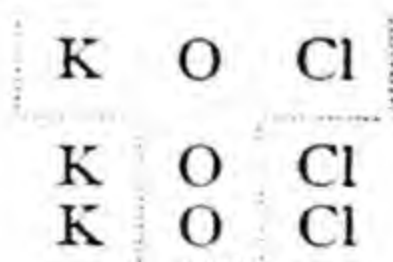
Wool and straw must not be bleached with chlorine or hypochlorite, both of which destroy them, but with sulphur dioxide (*q.v.*) or hydrogen peroxide. Hydrogen peroxide is now also used for bleaching cotton. Before the use of bleaching materials, the fabric was simply exposed to air and light in fields; the process lasted several months and was expensive. In 1746 it cost 1s. 6d. to 2s. per lb. of material bleached.

Other bleaching materials besides chlorine, hydrogen peroxide and sulphur dioxide are sodium peroxide, magnesium peroxide, perborates (which occur in some washing and bleaching powders), and sodium hyposulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ , a powerful *reducing* agent). Oils are often bleached by treatment with fuller's earth, which absorbs the colouring matter, and charcoal is similarly used for bleaching sugar (see p. 409). These materials have, it will be seen, different actions in bleaching: (i) oxidation; (ii) reduction; (iii) formation of colourless compounds; (iv) absorption. Most bleaching substances are also antiseptics. Since bleaching powder solution may deposit specks of solid bleaching powder in the fabric, which cause rotting, a solution of sodium hypochlorite is often used in laundries. It may be prepared by electrolysis, or by adding sodium carbonate solution to a solution of bleaching powder and filtering:



Sodium hypochlorite is largely used in bleaching wood-pulp for the manufacture of paper.

**Chlorates.**—When *excess* of chlorine is passed into a concentrated solution of caustic potash or soda, the hypochlorite first produced is rapidly converted into a chlorate, and the temperature rises. Two molecules of hypochlorite may be regarded as oxidising a third molecule to chlorate, being themselves reduced to chloride:



Suitable apparatus is shown in Fig. 218. Chlorine is generated from manganese dioxide and hydrochloric acid in the flask, washed with a little water, and passed into concentrated caustic potash solution in the beaker. To prevent the delivery tube



becoming choked by the crystals separating, an inverted funnel is used. When the liquid smells strongly of chlorine, it is cooled, and decanted from the crystals. If the decanted liquid is evaporated and allowed to cool, cubic crystals separate. These consist of potassium chloride. The crystals obtained by decanting the original liquid are washed once or twice with a little

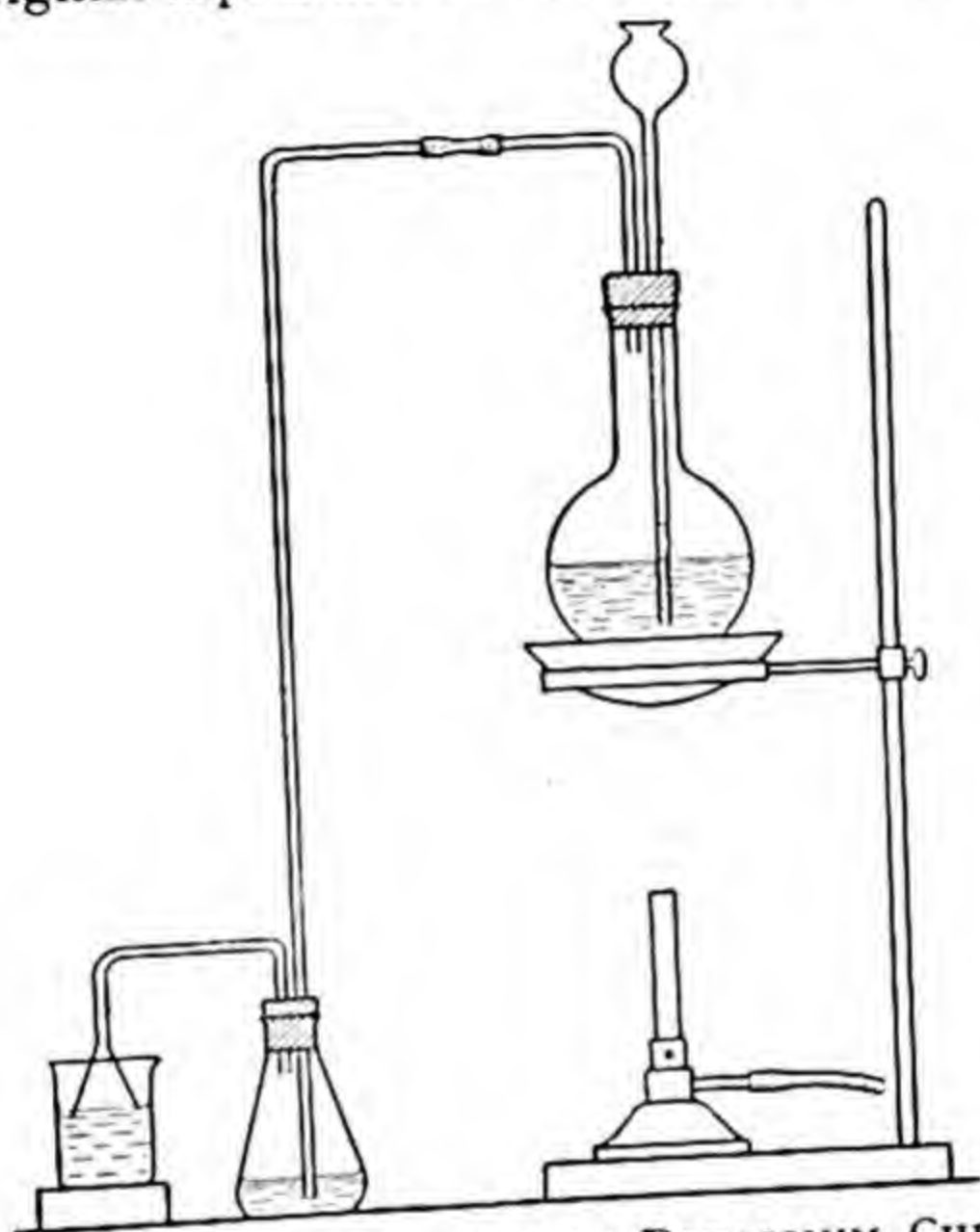
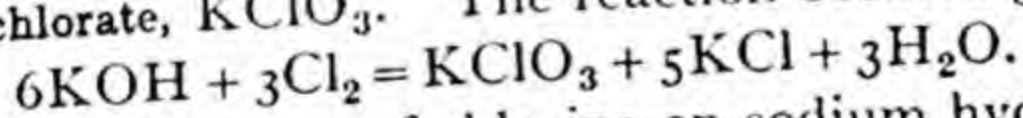
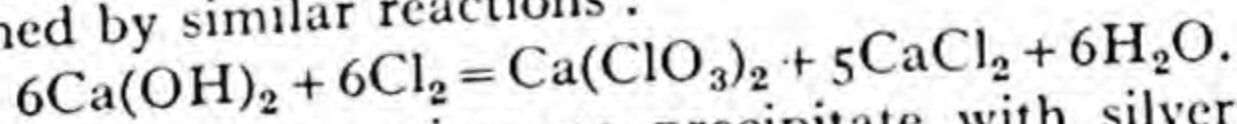


FIG. 218.—THE PREPARATION OF POTASSIUM CHLORATE.

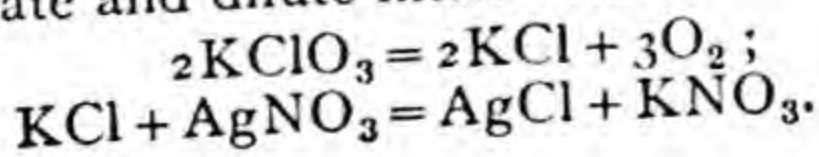
cold water and then recrystallised from hot water. They consist of potassium chlorate,  $\text{KClO}_3$ . The reaction occurring is :



By the action of excess of chlorine on sodium hydroxide solution (or milk of lime), sodium (or calcium) chlorate and chloride are formed by similar reactions :

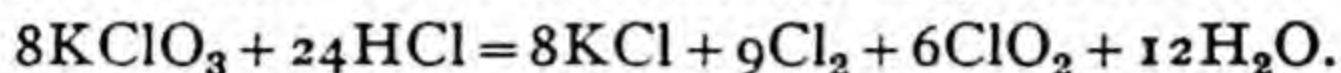


Potassium chlorate gives no precipitate with silver nitrate, but on heating it gives off oxygen, and the residue when dissolved in water gives a white curdy precipitate of silver chloride with silver nitrate and dilute nitric acid :



A little potassium chlorate treated with concentrated sulphuric acid in a test-tube turns orange-yellow, and evolves a yellow explosive gas, **chlorine dioxide**, having a peculiar odour. On warming there is a crackling noise, due to explosions of the gas, which has the formula  $\text{ClO}_2$ .

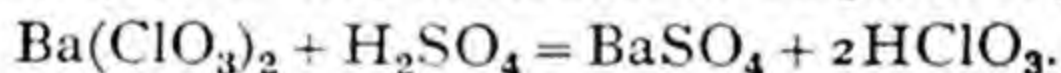
On warming potassium chlorate with concentrated hydrochloric acid, a greenish-yellow gas called *euchlorine*, which is a mixture of chlorine and chlorine dioxide, is evolved :



A mixture of potassium chlorate and sulphur explodes violently when struck with a hammer or ground in a mortar. If a few pieces of white phosphorus and some crystals of potassium chlorate are dropped into a glass of water, and a little concentrated sulphuric acid *cautiously* poured in through a thistle funnel, the phosphorus burns under water in flashes with a crackling noise, owing to oxidation by the chlorine dioxide liberated.

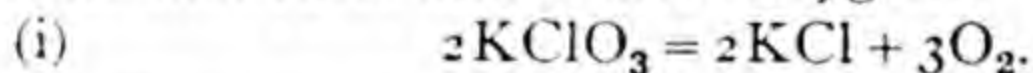
If a drop of concentrated sulphuric acid on the end of a glass rod is brought in contact with a mixture of powdered potassium chlorate with sugar or starch, the mass ignites and burns violently.

Barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$ , may be obtained by the action of sodium chlorate on barium chloride, and **chloric acid**,  $\text{HClO}_3$ , may be obtained in solution by acting upon a solution of barium chlorate with sulphuric acid when barium sulphate is precipitated:



It is a powerful oxidising agent, and is rather unstable.

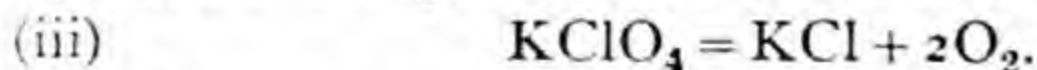
In the decomposition of potassium chlorate by heat, **potassium perchlorate**,  $\text{KClO}_4$ , is formed at an intermediate stage. The chlorate first fuses and evolves oxygen :



As the reaction proceeds, the evolution of oxygen slackens and the salt becomes pasty, owing to the formation of **potassium perchlorate**,  $\text{KClO}_4$  :



Potassium perchlorate is sparingly soluble in water and may be separated from the chloride by crystallisation. At a higher temperature the perchlorate fuses and evolves oxygen :



When decomposition is complete all is solid again, since potassium chloride melts only at a high temperature. Reactions (i)



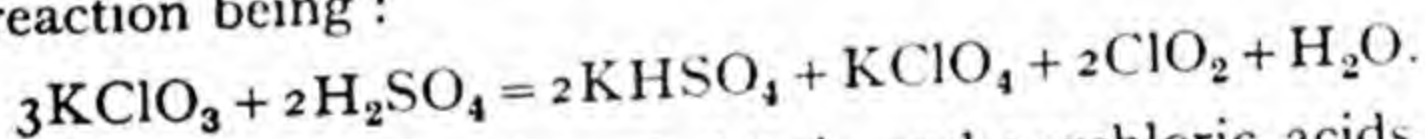
and (ii) proceed quite independently, and equations representing the decomposition of potassium chlorate with the formation of perchlorate, chloride and oxygen in definite proportions are incorrect.

When potassium perchlorate is distilled with concentrated sulphuric acid, perchloric acid,  $\text{HClO}_4$ , comes over as a fuming liquid, which is a powerful oxidising agent. It decomposes on standing and explodes on heating or in contact with charcoal when pure, but is very stable in concentrated solution in water.

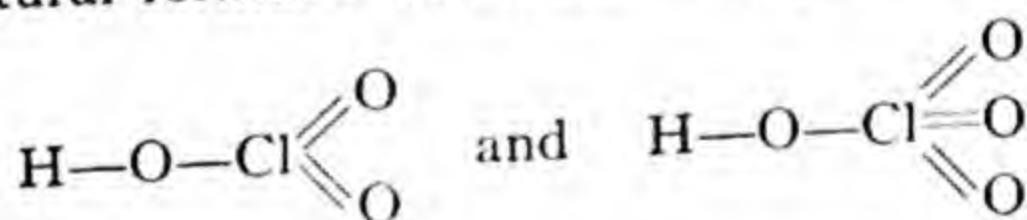
Chlorates and perchlorates are also produced by the *electrolysis* of hot saturated sodium chloride solution, between platinum electrodes placed close together. A little potassium chromate is added to improve the yield. The chloride is first completely converted into *chlorate*: on prolonged electrolysis, this passes into *perchlorate*. There are large chlorate works in Switzerland and at Niagara.

Chlorates are used as oxidising agents (e.g., in the oxidation of aniline to the dye aniline black), and in making fireworks. Perchlorates are employed in the manufacture of detonators and explosives.

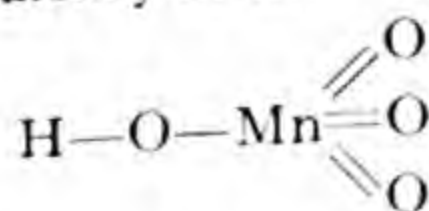
A perchlorate is also formed along with chlorine dioxide by the action of concentrated sulphuric acid on potassium chlorate, the reaction being :



The structural formulae of chloric and perchloric acids may be written :



in which the valency of the chlorine is 5 and 7, respectively. In permanganic acid the valency of the manganese is also 7 :



and potassium permanganate,  $\text{KMnO}_4$ , is isomorphous with potassium perchlorate,  $\text{KClO}_4$ . Chlorine and manganese both belong to Group VII in the periodic table (p. 235).

## CHAPTER XX

### BROMINE AND IODINE

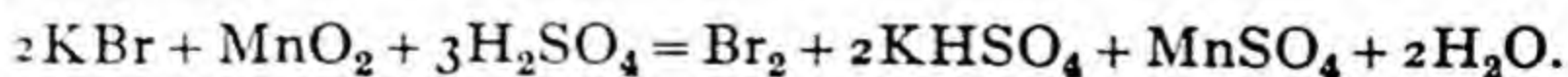
#### BROMINE

**Bromine.**—Potassium bromide,  $\text{KBr}$ , a salt used in medicine as a nerve sedative, contains the element bromine. Silver bromide,  $\text{AgBr}$ , is largely used in making photographic plates, films, and 'gaslight' paper. Compounds of bromine are therefore used in daily life fairly extensively. The free element is a dark red, heavy liquid giving a red vapour with a most irritating odour, hence its name (from the Greek *bromos*, a stench).

Bromine was discovered by Balard (1826) in the residues from the manufacture of salt at Montpellier. These liquors are known as *bittern*, and contain magnesium bromide,  $\text{MgBr}_2$ . When they are treated with chlorine a yellow colour is produced, due to liberation of free bromine. Bromine was at once recognised as a **halogen**, *i.e.*, an element of the same character as chlorine; its discovery was further evidence in favour of the elementary nature of the latter.

The source of the bromine of commerce is found in the bromides present in certain mineral springs, *e.g.*, the Ohio springs and some German springs, and the residues of the great potash deposits of Stassfurt. Magnesium bromide occurs in sea water; the Dead Sea (from which bromine is extracted) and the Great Salt Lake of Utah contain considerable quantities of bromides. Bromine compounds are found in sea animals and plants; the ancient Tyrian purple, obtained from a shellfish (p. 8), consists of dibromo-indigo.

The most important bromine compound in commerce is potassium bromide,  $\text{KBr}$ , and from this bromine can be obtained by heating with sulphuric acid and manganese dioxide in a retort (*cf.* chlorine):



It is condensed in a cool receiver as a dark red, nearly black, liquid (Fig. 219). It is better to condense the vapours under a little water in the receiver, as they are less likely to escape. The



bromine separates out as a heavy liquid, under a red layer of its aqueous solution (bromine water). Bromine vapour attacks the eyes powerfully, and the liquid has a corrosive action on the skin.

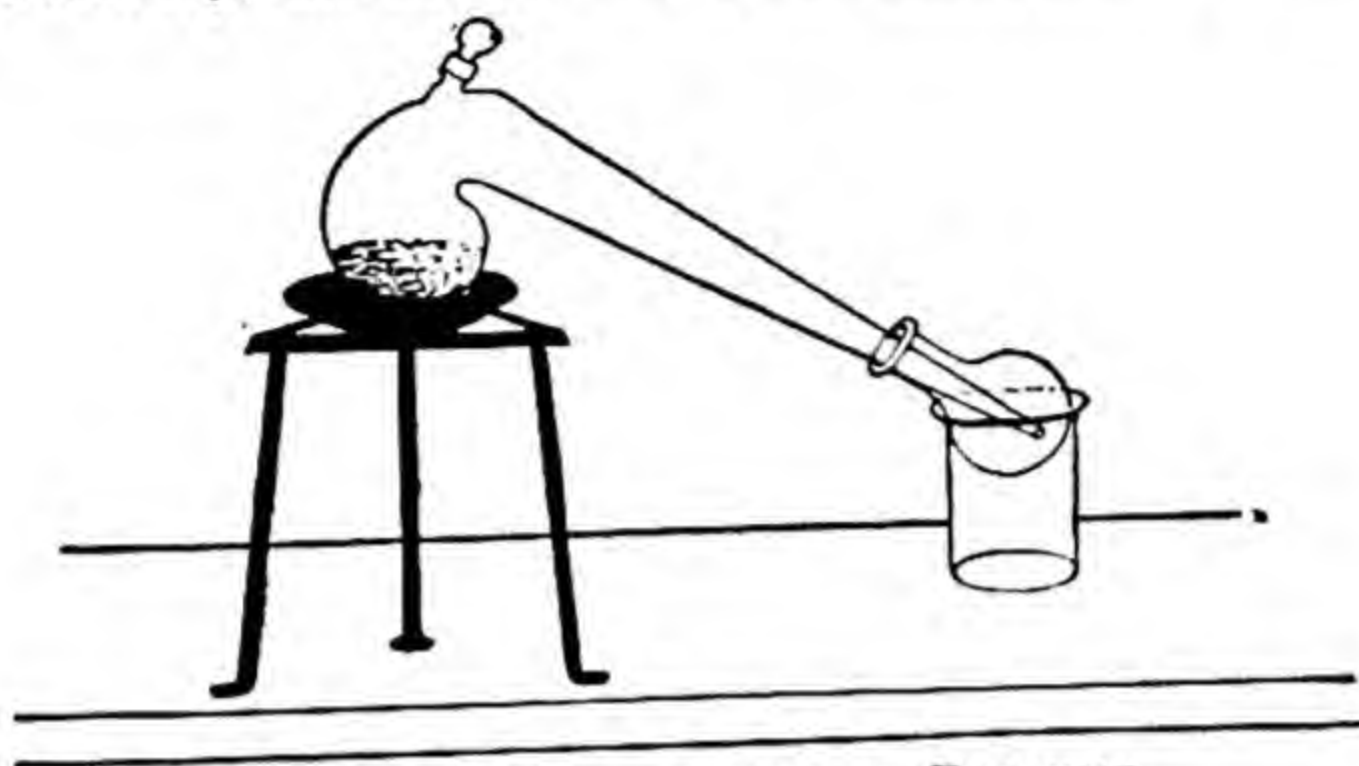
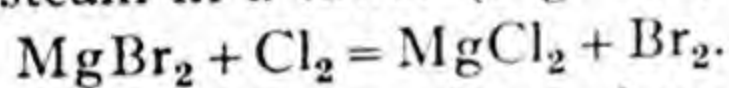


FIG. 219.—PREPARATION OF BROMINE.

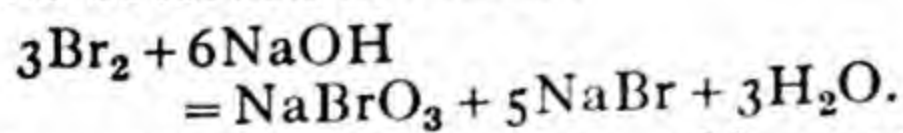
The element is poisonous. Bromine water has a feeble bleaching action, and possesses oxidising properties. It turns starch paste yellow.

Bromine is made from Stassfurt or Ohio brines by treating with chlorine and steam in a tower (Fig. 220):



The bromine vapour is condensed by cooling, and any passing on is caught by moist iron filings, when a solution of iron bromide is formed which is used in the preparation of potassium bromide (p. 334).

Much bromine is now made in the United States at Wilmington and other places from sea water, which is acidified and chlorinated. The bromine is blown out by a current of air and absorbed in alkali:



On acidifying the solution of bromate and bromide the bromine is set free:

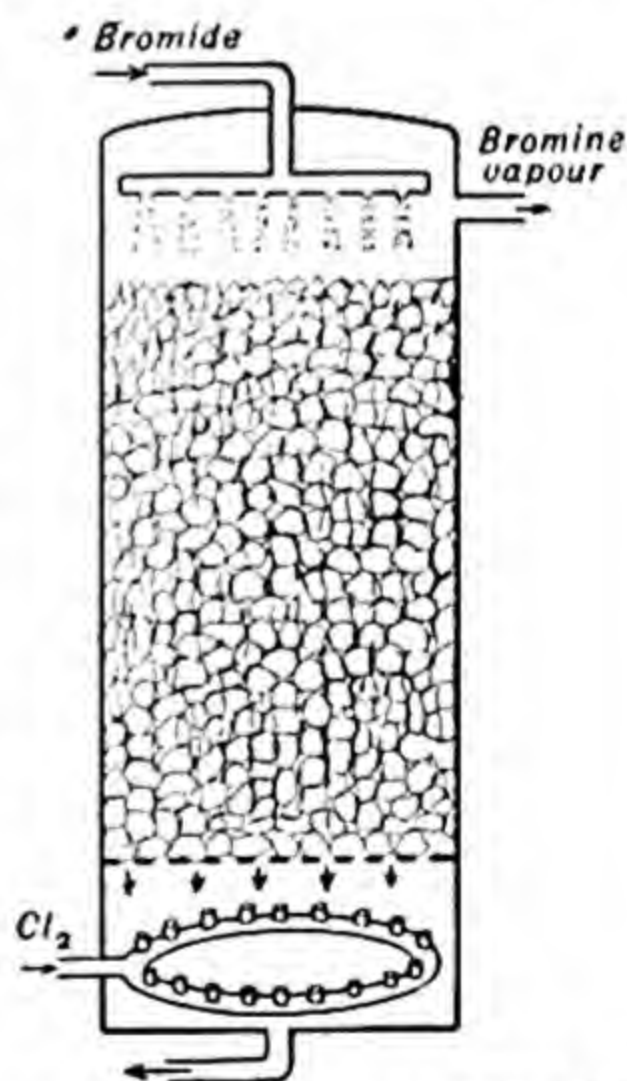
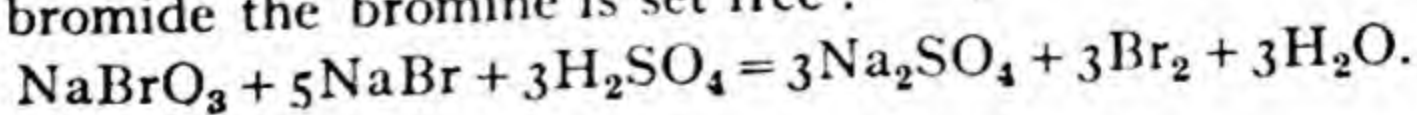
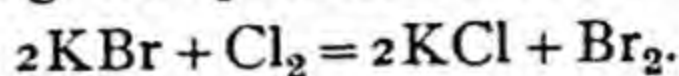


FIG. 220.—TECHNICAL PRODUCTION OF BROMINE.

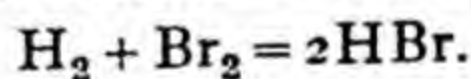
The bromine may be dried by shaking with concentrated sulphuric acid, and any chlorine present in it as an impurity may be removed by distilling over potassium bromide :



Bromine explodes in contact with white phosphorus ; red phosphorus burns in bromine vapour forming phosphorus tribromide,  $\text{PBr}_3$ , and pentabromide,  $\text{PBr}_5$ . Bromine also explodes in contact with potassium but does not act on sodium

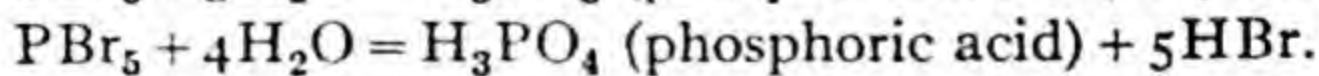
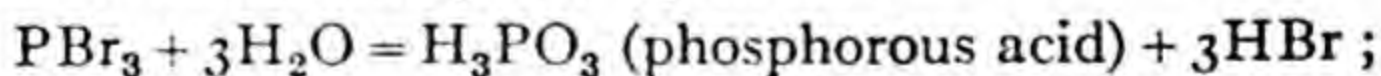
in the cold. The element is used in making bromides, certain dyes, and ethylene bromide for 'ethyl petrol.'

**Hydrogen bromide, or hydrobromic acid.**—Hydrogen and bromine vapours do not combine at all readily, but when the mixture is passed over heated platinum (a catalyst), gaseous hydrogen bromide is formed :



Another method of preparation is to drop bromine *cautiously* on

a paste of *red* phosphorus and water in a flask and pass the gas over moist red phosphorus in a U-tube to remove bromine vapour. The gas is collected by downward displacement (Fig. 221). Phosphorous tribromide and pentabromide are first formed and then decomposed by water :



Hydrobromic acid cannot be prepared in a state of purity by heating potassium bromide with concentrated sulphuric acid, since the gas is then much contaminated with bromine vapour, formed by the oxidation of hydrogen bromide by the hot, concentrated, sulphuric acid, which is reduced to sulphur dioxide :

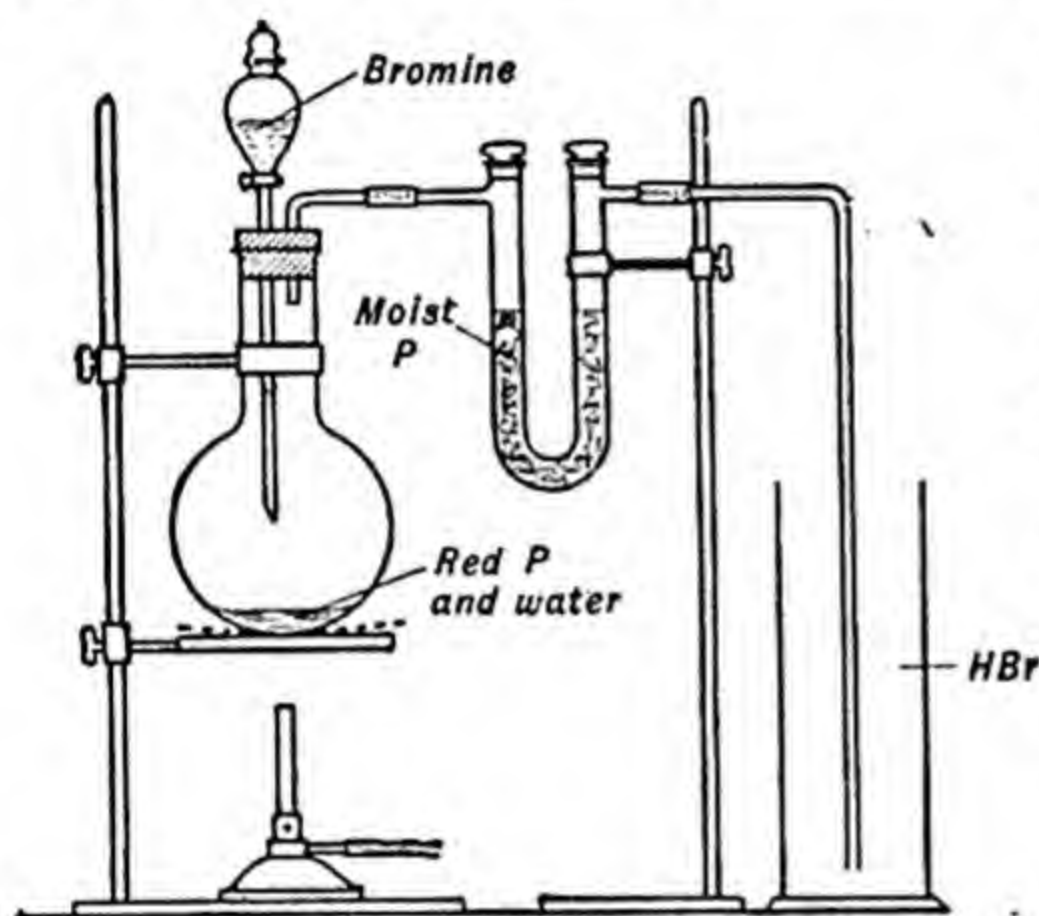
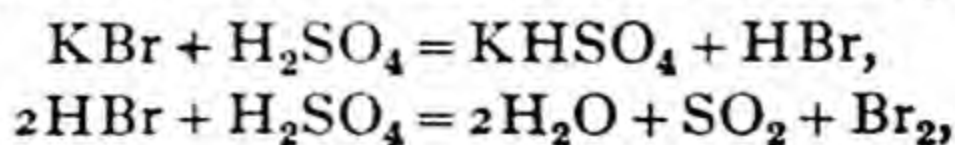


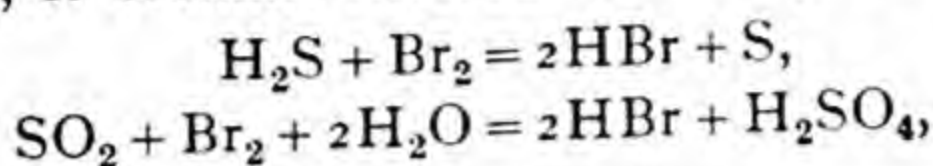
FIG. 221.—PREPARATION OF HYDROGEN BROMIDE.



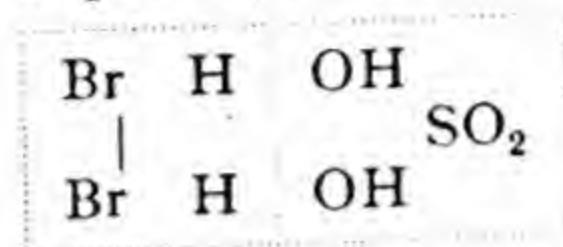
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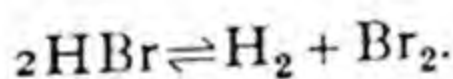
A *solution* of hydrobromic acid may be prepared by passing either sulphuretted hydrogen or sulphur dioxide through bromine water, or bromine covered with a layer of water :



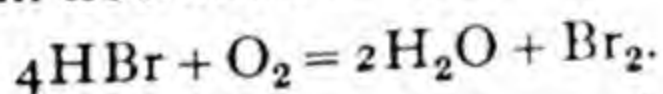
or



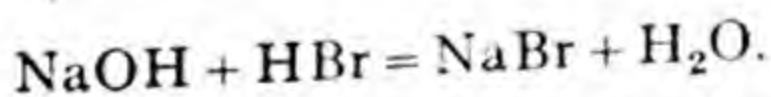
Hydrogen bromide is a colourless gas, with an irritating acid smell ; it is heavier than air, fumes strongly in moist air, and is very readily soluble in water to form an acid solution. It may be condensed to a colourless liquid, and even a solid, by strong cooling. The gas is less stable than hydrogen chloride, and dissociates, but only slightly, when strongly heated, with liberation of bromine :



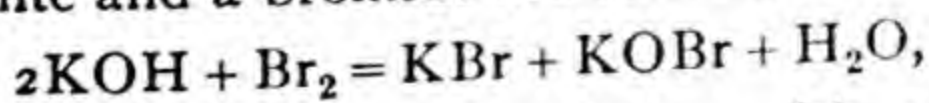
The solution oxidises slowly when exposed to air and light, and becomes yellow from liberation of bromine :



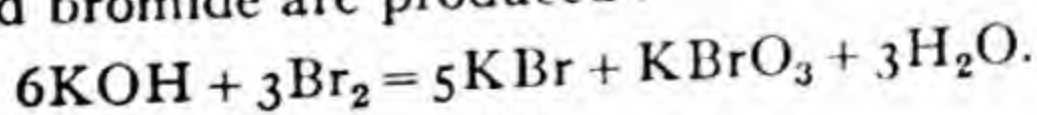
Aqueous hydrobromic acid dissolves metals with evolution of hydrogen and reacts with oxides, hydroxides or carbonates to form *bromides* :



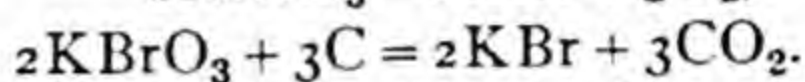
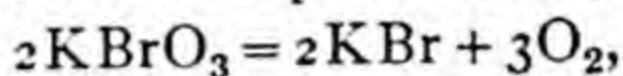
**Bromides.**—Bromides can also be obtained from bromine, and this method is used on the technical scale. It is most important to remember, however, that neither bromides nor iodides (*q.v.*) can be obtained *directly* in the pure state by the action of the element on caustic alkalies. The action is similar to that of chlorine : in the cold with excess of alkali an unstable hypobromite and a bromide are formed :



whilst in hot concentrated solution with excess of bromine, bromate and bromide are produced :

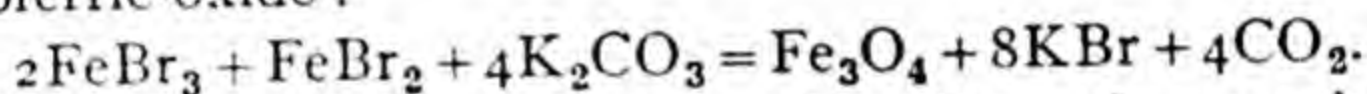


**Potassium bromate**,  $\text{KBrO}_3$ , is sparingly soluble and crystallises out of solution. If heated *strongly* it decomposes into bromide and oxygen: a perbromate is not formed (*cf.* chlorate). If the object is to prepare a *bromide*, therefore, the mixture of bromide and bromate obtained by the action of bromine on caustic potash solution is evaporated to dryness and the residue is heated, either alone, or, better, with powdered charcoal (when the bromate is decomposed at a lower temperature):



The mass is dissolved in water, filtered from excess of charcoal, evaporated and crystallised.

A solution of bromides of iron formed on shaking iron filings with bromine and water is treated with potassium carbonate, and the solution of potassium bromide filtered from the hydrated ferrosiferrous oxide:



A solution of a bromide gives with silver nitrate solution a yellowish-white precipitate of **silver bromide**,  $\text{AgBr}$ , insoluble in dilute nitric acid and only sparingly soluble in ammonia.

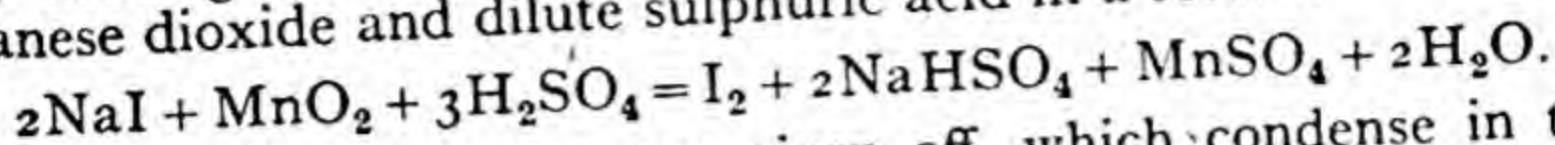
### IODINE.

**Iodine.**—The element iodine (pronounced *i-o-deen*) is familiar: a dark brown solution in alcohol is *tincture of iodine*, used as an antiseptic. Iodine was discovered by Courtois, in Paris, in 1811, but was first carefully investigated by Davy and by Gay-Lussac in 1813. Iodine occurs as organic compounds in cod-liver oil and in the thyroid gland. Iodides are supposed to be essential to health and a defect of iodine is said to produce diseases such as goitre. The normal iodine content of the body is assumed to be derived partly from food and partly from iodides in the sea spray carried inland by winds. Certain mineral waters contain iodides, *e.g.*, that of Woodhall Spa contains about 8 milligrams of potassium iodide per litre, and 'iodised salt' for table use is stated to contain sodium iodide. Foods containing traces of iodine are milk, butter, and green vegetables.

Iodine occurs in combination with metals as iodides in sea water. Seaweeds and sponges extract iodine from the water, and the ash of seaweed, called *kelp* or *varec*, contains iodides from which iodine is extracted. A small quantity of **sodium iodate**,  $\text{NaIO}_3$ , is present in *caliche*, the natural sodium nitrate of Chile.



**Preparation of iodine.**—Iodine is prepared in the laboratory by heating a mixture of sodium (or potassium) iodide, manganese dioxide and dilute sulphuric acid in a retort :



Beautiful violet vapours are given off, which condense in the cool neck of the retort and in the receiver as glittering black or grey scales of iodine, with a characteristic odour.

On the technical scale iodine is obtained from the iodides contained in *kelp*, which contains also sodium and potassium chlorides, sulphates, and carbonates, and some magnesium salts.

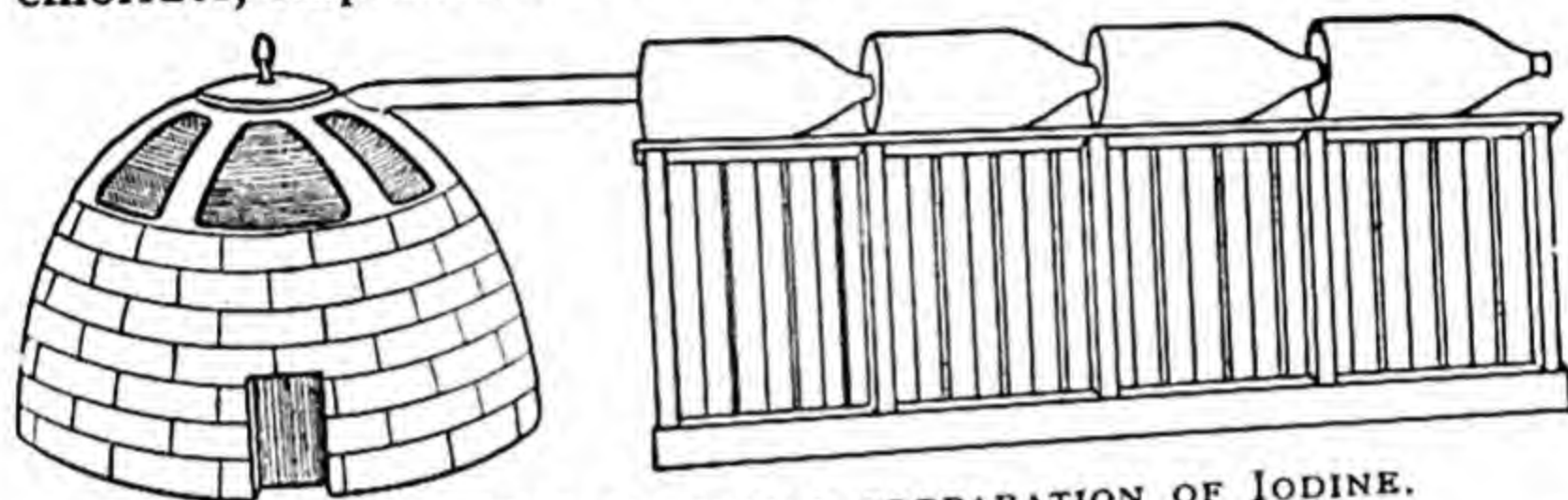
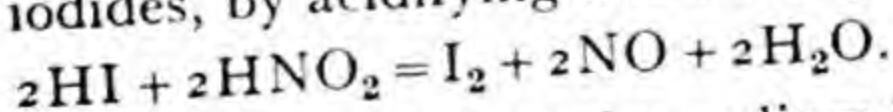


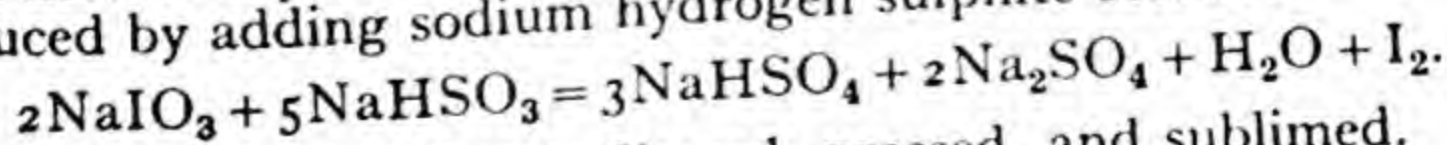
FIG. 222.—THE TECHNICAL PREPARATION OF IODINE.

These are separated by heating with water, filtering from the charcoal also present, and concentrating. The impurities largely crystallise out. The solution of iodides is then mixed with concentrated sulphuric acid and manganese dioxide in cast-iron retorts with lead covers, and the iodine which passes over is collected in stoneware receivers called *aludels* (Fig. 222). It is washed with cold water, in which iodine is only slightly soluble, dried and sublimed, when it forms black steel-like glittering crystals. It may be purified still further by re-subliming it mixed with potassium iodide. In a more modern process the seaweed is not burnt but is extracted with sodium carbonate to remove iodide, and the residue can be used in preparing adhesives (*algin*).

Iodine is extracted from brines from oil wells in California, which contain iodides, by acidifying and adding sodium nitrite :



The mother-liquor from *caliche* contains sodium iodate, which is reduced by adding sodium hydrogen sulphite solution :



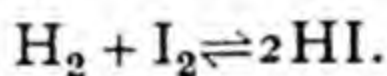
The precipitated iodine is filtered, pressed, and sublimed.

Iodine vapour dissociates on heating,  $I_2 \rightleftharpoons 2I$ , as is shown by the vapour density.

Iodine is only slightly soluble in water, forming a yellowish-brown solution. It dissolves readily in hydriodic acid or potassium iodide solutions, forming deep brown, nearly black, liquids. It also dissolves in alcohol and ether to form brown solutions, and in carbon disulphide and chloroform to form violet solutions, having the same colour as the vapour.

The most delicate *test for iodine* is the deep blue colour which a trace of it gives with a solution of starch. The colour disappears on heating the solution but reappears on cooling. Iodine also gives a blue colour with solid starch, so that paper (sized with starch) and starched linen are usually turned blue by iodine.

**Hydrogen iodide, or hydriodic acid.**—Hydrogen and iodine vapour combine to a certain extent in presence of heated platinum (a catalyst), but the reaction is incomplete and hydrogen iodide is easily dissociated by heat:



The gas is best prepared by dropping water on a mixture of iodine and red phosphorus in a flask (Fig. 223) and collecting by downward displacement:

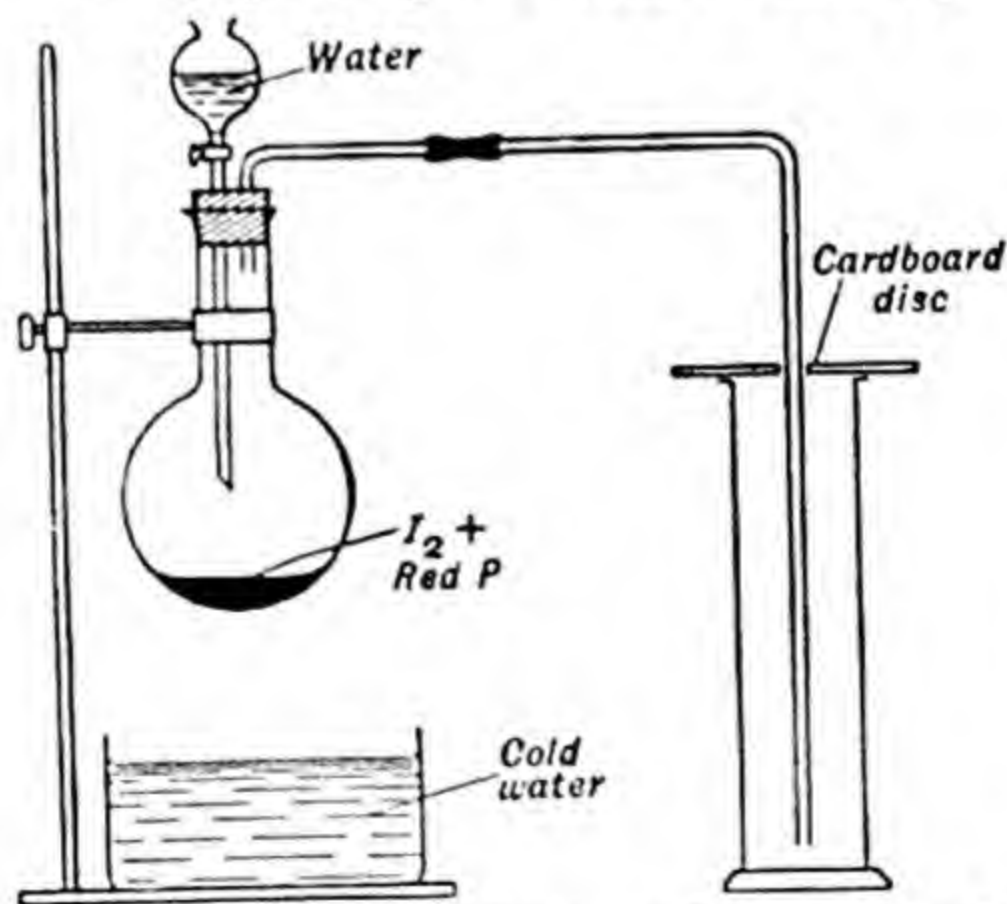
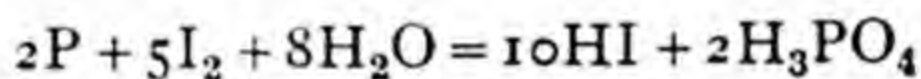
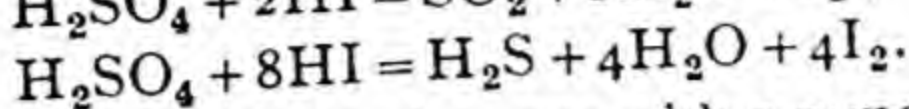
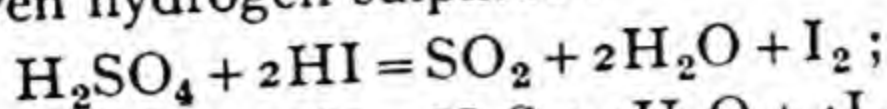


FIG. 223.—THE PREPARATION OF HYDROGEN IODIDE.

Hydrogen iodide cannot be prepared in a pure state by heating potassium iodide with sulphuric acid, since the latter oxidises it



to iodine, and is reduced to sulphur dioxide (*cf.* hydrogen bromide) or even hydrogen sulphide :

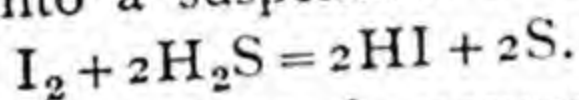


Hydrogen iodide is a colourless gas with a pungent acid smell, which fumes strongly in moist air and is very soluble in water. It is easily decomposed by heat or on exposure to sunlight, iodine being set free :  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ .

It is more easily liquefied than hydrogen chloride or bromide.

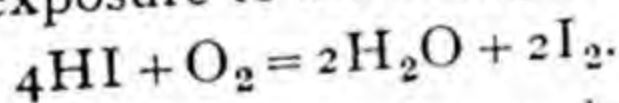
The composition of hydrogen iodide (or bromide) may be determined by the action of sodium amalgam on the dry gas, as explained in the case of hydrogen chloride (p. 322).

An aqueous solution of hydriodic acid is obtained by passing hydrogen sulphide into a suspension of iodine in water :

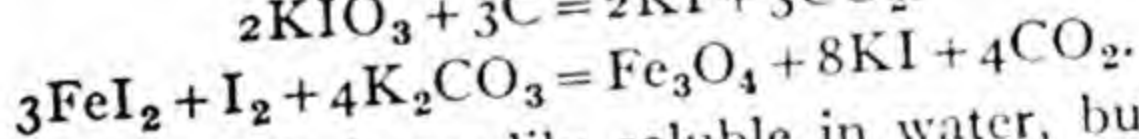
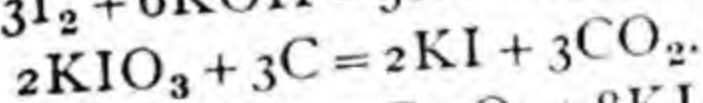
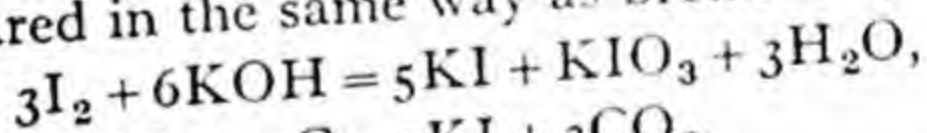


The action ceases when a certain concentration of hydriodic acid is produced, but a concentrated solution may be obtained by distilling the more dilute solution so obtained. Mainly water distils over at first, then the temperature rises to  $127^\circ$  and a constant boiling solution (p. 321) containing 57 per cent. of hydriodic acid distils over.

Hydriodic acid differs from hydrochloric and hydrobromic acids in being a strong reducing agent : the solution rapidly becomes brown on exposure to air owing to liberation of iodine :



**Iodides** are prepared in the same way as bromides (see p. 333) :



**Potassium iodide**,  $\text{KI}$ , is readily soluble in water, but **potassium iodate**,  $\text{KIO}_3$ , is sparingly soluble. A **periodate**,  $\text{KIO}_4$ , is formed on heating the iodate. Silver nitrate gives with soluble iodides a *light yellow* precipitate of **silver iodide**,  $\text{AgI}$ , insoluble in dilute nitric acid and also insoluble in ammonia.

Potassium iodide is applied medicinally, but since it acts much more powerfully than the bromide its use requires great care. The bromide and iodide are also used in photography (*q.v.*).

\***Fluorine**.—Besides chlorine, bromine, and iodine, there is another element belonging to the same group, viz. fluorine.

It occurs as the mineral *fluorspar*, calcium fluoride,  $\text{CaF}_2$ , used in metallurgy as a *flux*, and also in making *enamels*. When this is distilled with concentrated sulphuric acid, a liquid, **hydrofluoric acid**,  $\text{HF}$ , is obtained, which is used in etching glass, removing sand from castings, and (in the form of the soluble **sodium fluoride**,  $\text{NaF}$ ) as an antiseptic. The solution of glass and sand by the acid is due to the formation of **silicon fluoride**,  $\text{SiF}_4$ , a gas which is obtained by heating sand and powdered fluorspar with concentrated sulphuric acid. When passed into water it deposits gelatinous silica and forms a solution of **hydrofluosilicic acid**,  $\text{H}_2\text{SiF}_6$ .

The element fluorine is obtained by the electrolysis of anhydrous hydrofluoric acid to which a little potassium fluoride is added to render it conducting. It is a pale yellow gas which combines spontaneously with most elements and is the most active element known.

**\*The halogens.**—The group of elements **fluorine**, **chlorine**, **bromine** and **iodine** exhibit many similarities and are classed together as the **halogens** (Greek *hals* = salt). They are all coloured substances, they all have pungent, irritating odours, and their molecules all contain two atoms. Iodine vapour at high temperatures is dissociated into atoms:  $\text{I}_2 \rightleftharpoons 2\text{I}$ ; bromine and chlorine are probably also dissociated to a slight extent at very high temperatures. The elements are univalent, combining with and displacing hydrogen atom for atom. They combine readily with many non-metals and metals, and their compounds also show many points of resemblance. The halogens react with alkalis, forming chlorides, bromides, and iodides with hypochlorites, hypobromites and (possibly) hypoiodites when the alkali is in excess and the temperature is not allowed to rise, and chlorides, bromides, and iodides with chlorates, bromates, and iodates when the halogen is in excess and the temperature rises. All these compounds have analogous formulae. (Fluorine reacts differently with alkalis, an oxide,  $\text{F}_2\text{O}$ , and an alkali fluoride being formed.) Chlorides, bromides, and iodides all give precipitates with silver nitrate solution and the silver salts darken on exposure to light.

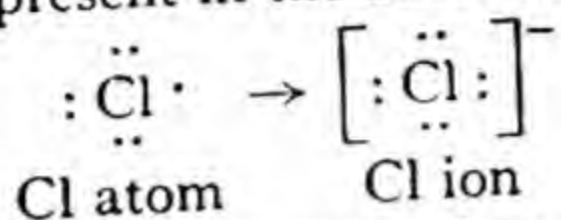
The similarity in properties of the halogens is to be expected from their position in the periodic system of the elements, where they are classified together in the seventh group (p. 235). Their atomic numbers are as follows :

fluorine 9  
chlorine 17

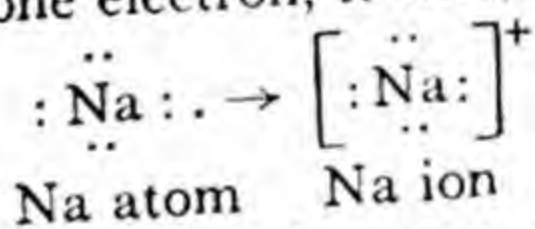
bromine 35  
iodine 53.



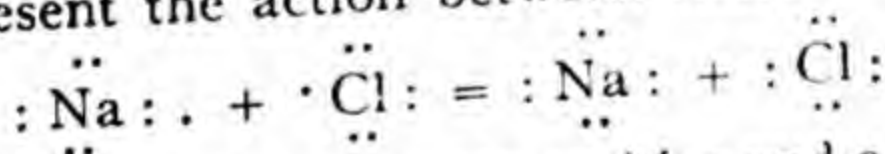
Since each halogen comes before an inert gas element, the atom of which contains an *outer* stable group of eight electrons (p. 249), and since the outer group is built up as we pass from left to right in the periods, we may infer that the atoms of the halogens contain outer groups of *seven* electrons. They therefore exhibit a tendency to take up one more electron to form an outer octet, which will be present in the **halide ion** :



The ion contains one electron more than the neutral atom, and has therefore unit negative charge,  $\text{Cl}^{-}$ . This extra electron may be taken from a metal atom. For example, since sodium and potassium occur in the first group, just after an inert gas, we may assume that their atoms have commenced to build up another outer layer of electrons over and above the octet of the inert gas, and that they contain an outer layer of *one* electron only. This lone electron is easily lost to the halogen atom and the residue of the alkali metal atom forms an ion with a stable grouping of eight outer electrons (which were within the outer single electron), and since this ion is formed from the neutral atom by the loss of one electron, it carries unit positive charge :

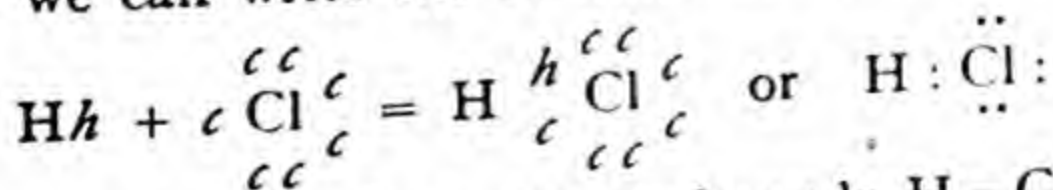


Thus we represent the action between sodium and chlorine as follows :



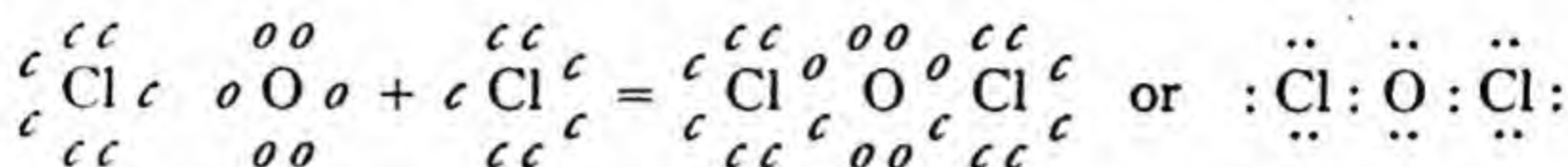
The ions so produced are separate entities and are held together in the crystal by electrostatic attraction only, without any true valency bond (p. 190).

The halogen hydracids, on the other hand, are true covalent compounds (p. 250) and are formed by the *sharing of a pair of electrons*, one from the hydrogen atom and one from the chlorine, or other halogen atom, to form a covalent link. Let us represent the hydrogen outer electron by *h* and the chlorine outer electrons by *c*, then we can write the formula of hydrogen chloride as follows :



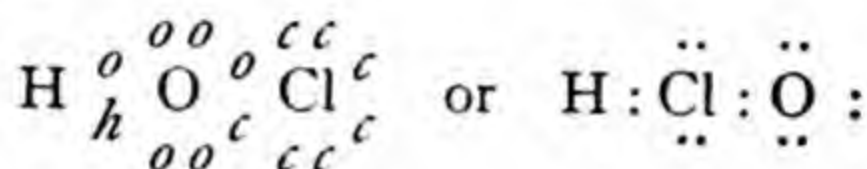
which corresponds with the ordinary formula  $\text{H} - \text{Cl}$ .

The oxygen atom has six outer electrons and can take up two more to form a stable octet. It can also *share* two, one from each chlorine atom, to form chlorine monoxide :



which is ordinarily written Cl – O – Cl. Each atom is surrounded by eight electrons.

In a similar way we may write the electronic formula of hypochlorous acid as :



This can ionise into  $\text{H}^+$  and  $[\text{:}\ddot{\text{Cl}}:\ddot{\text{O}}\text{:}]^-$ .



## CHAPTER XXI

### SULPHUR AND ITS COMPOUNDS

**Sulphur and its compounds.**—Sulphur is one of the best known non-metallic elements, and its compounds have many important technical uses. The free element, commonly called *brimstone* (from the old German *Brennstein*, 'combustible stone'—the modern German name is *Schwefel*) is used in vulcanising rubber and in dressing vines to prevent disease. Free sulphur occurs in large quantities in Sicily, and it was therefore known to the Greeks and Romans. Homer (about 900 B.C.) mentions the use of burning sulphur in fumigation and the gas sulphur dioxide,  $\text{SO}_2$ , formed by burning sulphur in air, was used in bleaching and purifying cloth. A picture of a sulphur pan and a beehive-shaped frame on which cloths could be hung over the pan, was found at Pompeii. The curious flame and pungent fumes of burning sulphur were supposed to scare away demons.

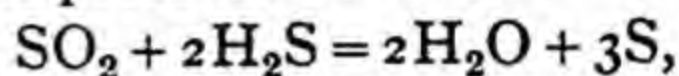
Sulphur dioxide is an acidic anhydride, and the salts of sulphurous acid, especially calcium bisulphite,  $\text{Ca}(\text{HSO}_3)_2$ , are very largely used in preparing wood-pulp for the manufacture of paper. By the oxidation of sulphur dioxide, obtained by burning sulphur or iron pyrites,  $\text{FeS}_2$ , sulphuric acid,  $\text{H}_2\text{SO}_4$ , the most important compound of sulphur, is manufactured in immense quantities and put to a large number of uses. Less important compounds of sulphur, which find technical applications, are carbon disulphide,  $\text{CS}_2$ , sulphur chloride,  $\text{S}_2\text{Cl}_2$  (used in vulcanising rubber in some processes), and sodium thiosulphate ('hypo'),  $\text{Na}_2\text{S}_2\text{O}_3$ , used in photography. (The Greek name for sulphur was *theion*.)

**Occurrence of sulphur.**—Sulphur occurs in Nature either free or in combination. Free sulphur occurs in large quantities in Italy in the volcanic regions of Sicily, and in America in the southern states of Louisiana and Texas.

In Sicily the sulphur occurs stratified with rock, mostly gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and limestone. It is found

occasionally in large, yellow, transparent crystals, but usually in crystalline masses. The sulphur in the craters of extinct

volcanoes is formed by the interaction of volcanic gases, containing hydrogen sulphide and sulphur dioxide, in presence of water :



but the sulphur deposits are supposed to have been formed by the reduction of gypsum (calcium sulphate) by organic matter :

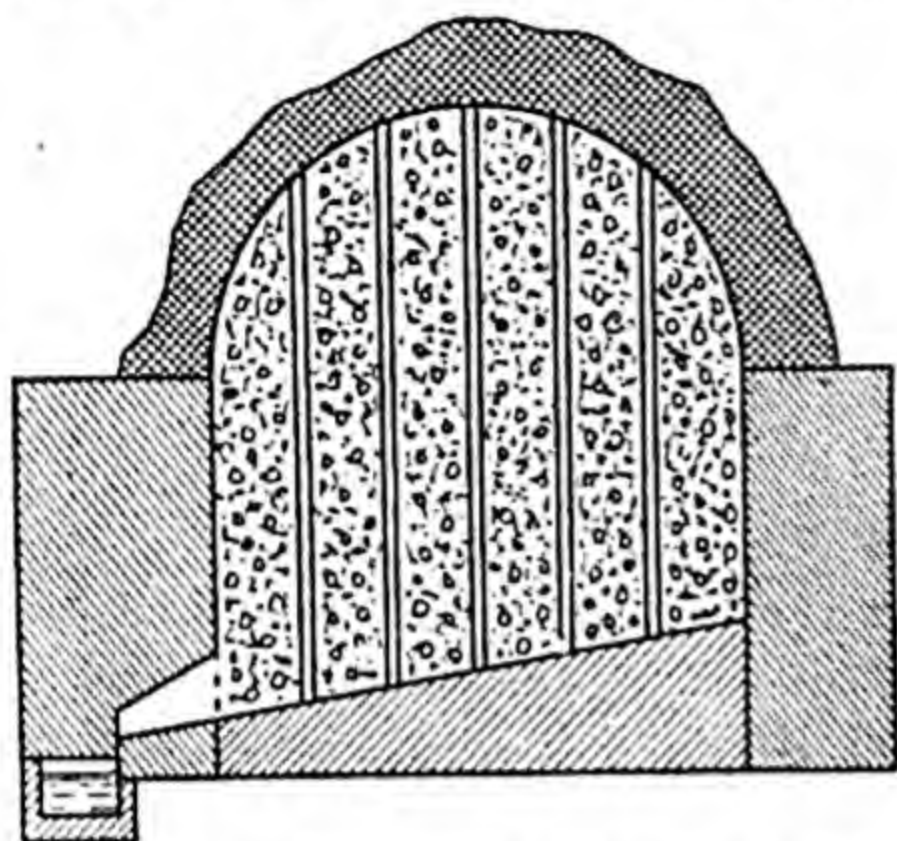
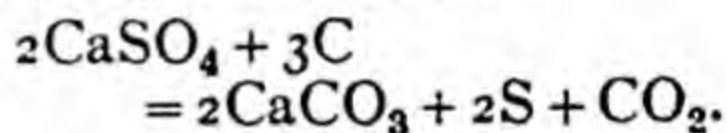


FIG. 224.—SICILIAN SULPHUR KILN.

many of which are important ores of metals (*i.e.*, serving for their extraction), *e.g.*, lead sulphide, or *galena*,  $\text{PbS}$ ; zinc sulphide, or *blende*,  $\text{ZnS}$ ; *copper pyrites*,  $\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$ ; and *iron pyrites*,  $\text{FeS}_2$  (used as a source of sulphuric acid). Large masses of *gypsum*, or calcium sulphate,  $\text{CaSO}_4, 2\text{H}_2\text{O}$ , and other **metallic sulphates**, are common. Sulphur is a constituent of some kinds of organic matter; thus the blackening of silver spoons by eggs is due to the sulphur contained in the albumin of the latter. It is found in certain bacteria, *e.g.*, *Beggiatoa alba*, which are capable of decomposing sulphur compounds in their life-processes. The pungent principles of onions, garlic, horse-radish, and mustard are organic sulphur compounds. Combined sulphur is present in hair and wool.

Combined sulphur occurs in the form of **metallic sulphides**,

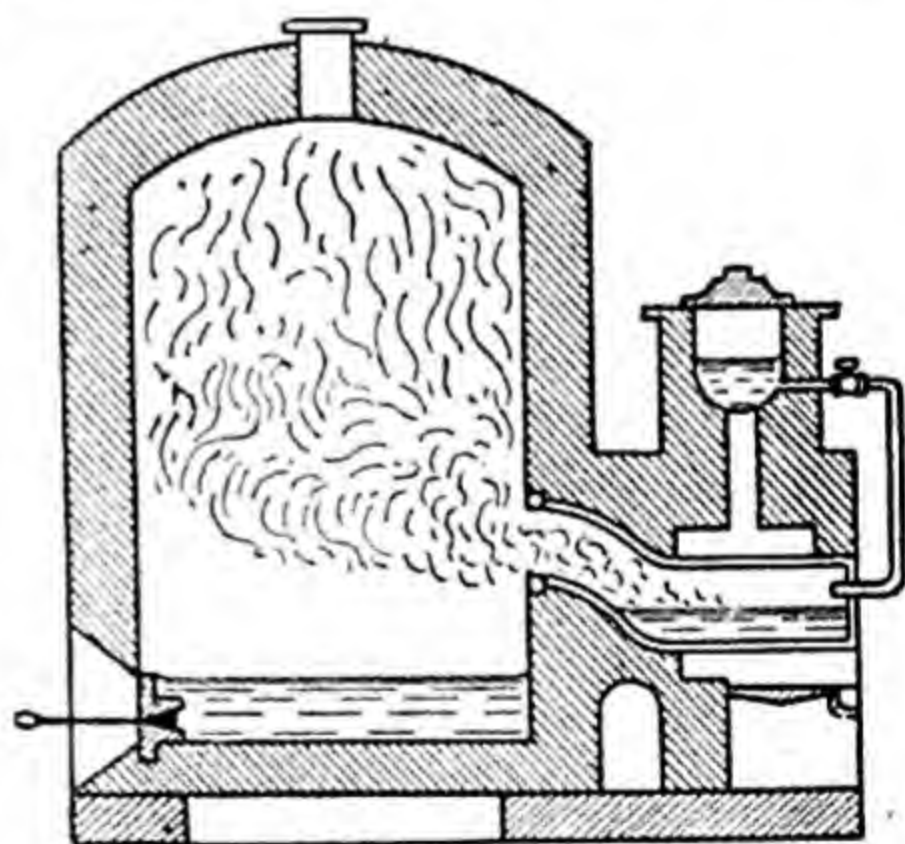


FIG. 225.—REFINING SULPHUR BY DISTILLATION.

**The technical preparation of sulphur.**—Native sulphur in Sicily is stacked in lumps in brick kilns, called *calcaroni*, built on sloping hillsides, with air spaces, and covered with powdered

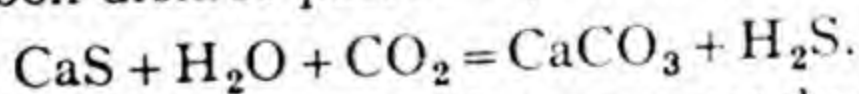


ore (Fig. 224). The ore is kindled at the top, and the heat of combustion of part of the sulphur serves to melt the remainder, which flows off into wooden moulds. This seems rather a wasteful process, but coal is very expensive in Italy and it is cheaper to burn part of the sulphur than to use other fuel.

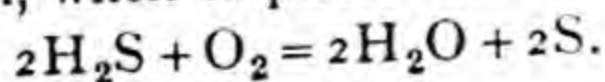
Sicilian sulphur is refined at Marseilles, where fuel is cheaper, with the apparatus shown in Fig. 225. The sulphur is fused in an iron pot, whence it flows into an iron retort, heated over a fire. The sulphur boils, and the vapour is conducted into a large brickwork chamber. At first the vapour condenses on the cold walls as a light yellow crystalline powder, called *flowers of sulphur*. As the walls become hot, this melts (unless it is removed), and runs down as a liquid to the bottom, whence it is tapped off into cylindrical moulds, to form *roll sulphur*, or *brimstone*.

The Frasch process of extraction used in America is different. The deposit occurs below clay, quicksand, and rock. A boring is made to the deposit, and three concentric pipes are sunk (Fig. 226). Down the outer pipe superheated water is pumped. This fuses the sulphur. Air is then forced down the inner pipe, when an emulsion of molten sulphur and air bubbles rises to the surface through the remaining annular space. This passes to large wooden vats, where the sulphur solidifies, and is ready for immediate use. America now produces 80 per cent. of the total sulphur used in the world.

Sulphur is also extracted from the calcium sulphide of *alkali waste* from the Leblanc process (p. 574). This is suspended in water and carbon dioxide passed in, when hydrogen sulphide is evolved :



Air is added and the gas passed over a catalyst composed of heated oxide of iron, when sulphur is formed :



This is called the *Chance-Claus process*.

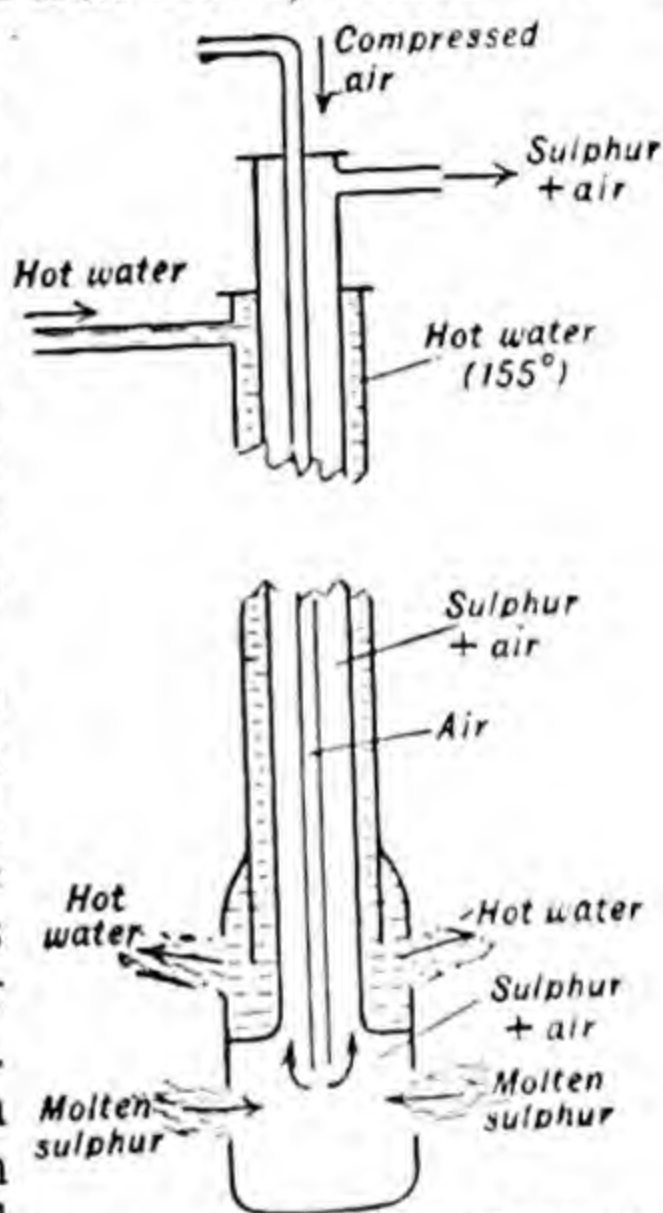
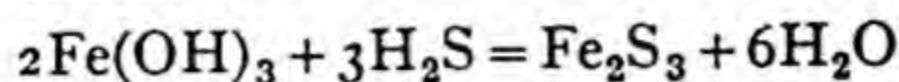
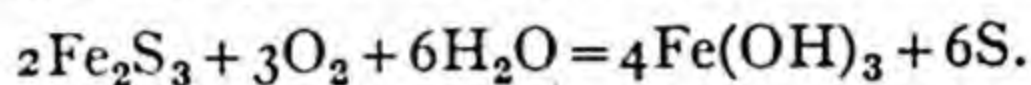


FIG. 226.—THE FRASCH SULPHUR PUMP.

Sulphur is separated in the purification of crude coal gas, which contains hydrogen sulphide. The gas is passed through boxes containing hydrated ferric oxide ('bog iron ore'), when ferric sulphide is formed :



The spent mass is exposed to air, when oxidation occurs :



When the mass has been used several times the spent oxide is burnt in a current of air and the sulphur dioxide formed is used to manufacture sulphuric acid.

Sulphur is also extracted from gases containing sulphur dioxide and formed in roasting ores and smelting metals, for example in roasting zinc blende :  $2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2$ . The sulphur dioxide is dissolved from the gas by a suitable solvent, from which it is expelled by heating, and is passed over strongly heated coke, when it is reduced to sulphur :  $\text{SO}_2 + \text{C} = \text{CO}_2 + \text{S}$ .

It is often more convenient to use the sulphur dioxide in roaster and smelter gases by converting it into sulphuric acid, which is mostly done by purifying the gas and oxidising the sulphur dioxide in it by the contact process (p. 356).

**The allotropic forms of sulphur.**—Sulphur, carbon (pp. 57, 403), and phosphorus (p. 456), are examples of non-metallic elements which exist in different solid forms with characteristic properties. These, it will be recalled (see p. 56), are known as *allotropic forms* of the element, and the existence of these forms is called *allotropy*. Some metals, such as tin (p. 57), also exist in allotropic forms. Allotropic forms differ in physical properties, such as density, and also in chemical properties, some forms being chemically more reactive than others : white and red phosphorus are notable in this respect.

The allotropic forms of sulphur comprise two different crystalline forms : (1) rhombic sulphur (or  $\alpha$ -sulphur), the crystalline form of which is shown in Fig. 228 ; and (2) monoclinic sulphur (or  $\beta$ -sulphur), the crystalline form of which is shown in Fig. 229. Sulphur also exists in different amorphous (non-crystalline) forms, the best known being *plastic sulphur* (Fig. 230), and *milk of sulphur*, a white amorphous powder. All these varieties give the same products in chemical reactions, e.g. the same weight of sulphur dioxide on oxidation.

Rhombic or  $\alpha$ -sulphur, the common form, is prepared by allowing a solution of roll sulphur in carbon disulphide slowly



to evaporate, when pale-yellow transparent crystals are formed, giving a lemon-yellow powder. The density of  $\alpha$ -sulphur is 2.06, and its melting point is  $113^{\circ}$ . It is insoluble in water, but freely soluble in carbon disulphide. Rhombic sulphur is *the stable form at the ordinary temperature, and all the other forms pass into it on standing*. Roll sulphur consists almost entirely

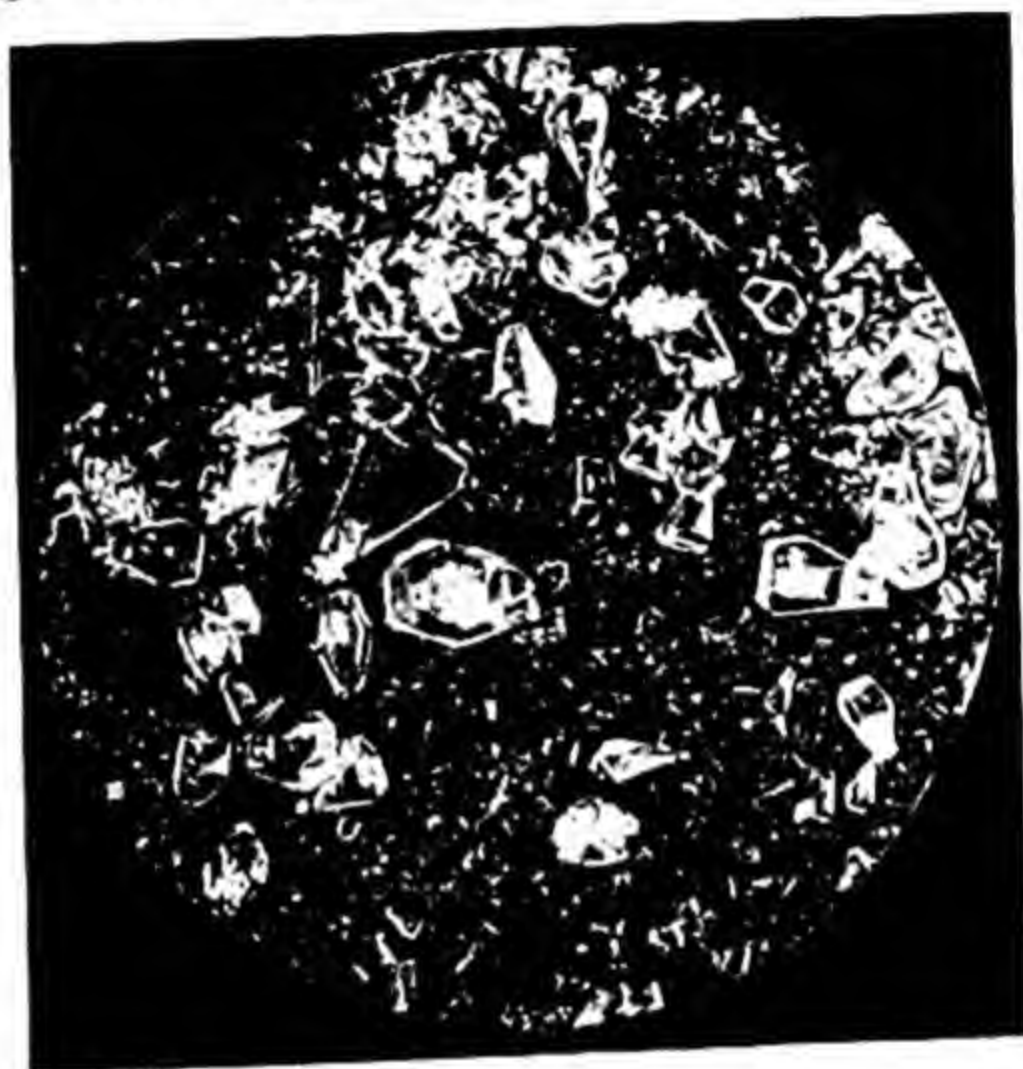
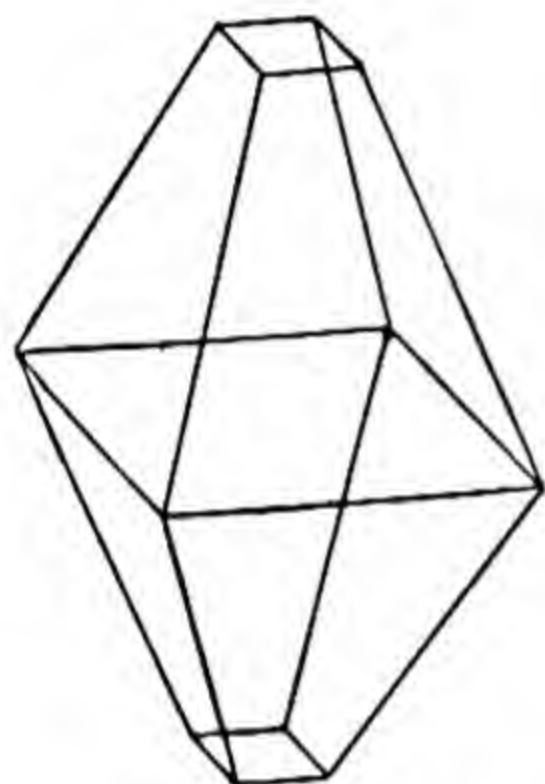


FIG. 228.—RHOMBIC SULPHUR CRYSTALS.

of rhombic sulphur ; flowers of sulphur are principally composed of it, but contain also a white amorphous variety insoluble in carbon disulphide.\*

**Monoclinic or  $\beta$ -sulphur**, discovered in 1823 by Mitscherlich, is produced when fused sulphur is allowed to crystallise.

A dish is half filled with small pieces of roll sulphur, and heated slowly on a sand-bath till the whole is just fused. It is allowed to cool until a crust forms on the surface, when two holes are made in this crust (one to admit air) with a pointed glass rod, and the still liquid portion poured off. When the crust is removed, the inside of the dish will be found to be lined with transparent needle-shaped crystals of  $\beta$ -sulphur (Fig. 229), having a deeper yellow colour than  $\alpha$ -sulphur. On standing for a few days, the crystals become opaque and brittle, and the

\* Roll sulphur and flowers of sulphur are *not* allotropic forms of sulphur : they are *commercial forms*.

colour becomes lemon-yellow. The crystals now consist of aggregates of minute crystals of  $\alpha$ -sulphur, although the original monoclinic form is preserved by the whole crystal. The gradual transition from one form to the other is readily followed by the colour.

$\beta$ -sulphur, when quickly heated, melts at  $119^\circ$ , and has a density of 1.96. It is insoluble in water, but soluble in carbon disulphide; the solution on evaporation deposits  $\alpha$ -sulphur, the stable form at room temperature.

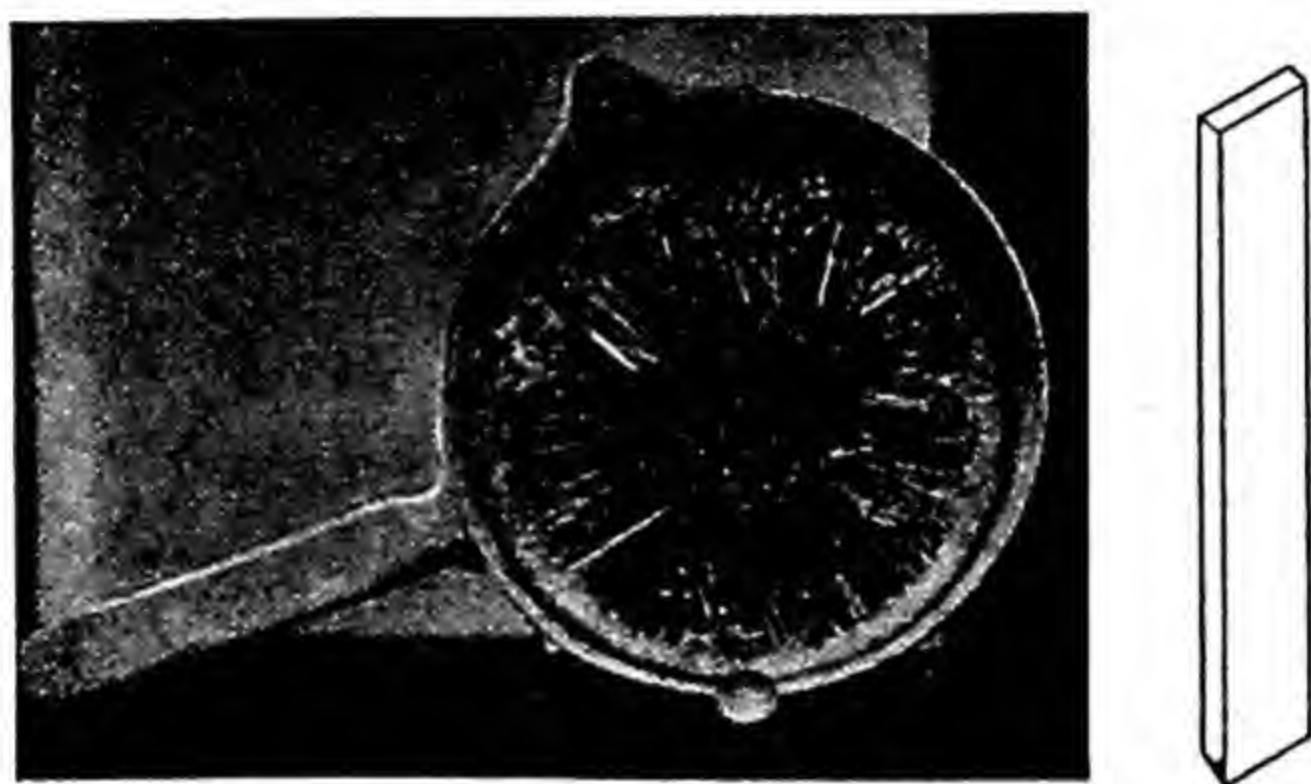
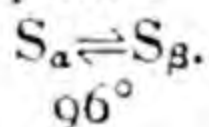


FIG. 229.—MONOCLINIC SULPHUR CRYSTALS.

(By courtesy of D. van Nostrand Co.)

When  $\alpha$ -sulphur is heated for a long time above  $96^\circ$ , say in boiling water, it changes into  $\beta$ -sulphur, whilst below this temperature  $\beta$ -sulphur changes slowly into  $\alpha$ -sulphur. The two forms are in equilibrium at  $96^\circ$ , which is called the **transition point** for the two forms of sulphur:



When  $\alpha$ -sulphur is *rapidly* heated, it melts at  $113^\circ$ , before it has had time to change into  $\beta$ -sulphur. Between  $96^\circ$  and  $113^\circ$  it is in what is called a **metastable state**, as is  $\beta$ -sulphur below  $96^\circ$ .

**Plastic sulphur.**—The changes which sulphur undergoes when it is slowly heated to its boiling point are very interesting. It melts at  $113^\circ$ , forming a light orange-yellow mobile liquid which does not wet glass; on pouring this into water it solidifies to crystalline  $\beta$ -sulphur.\* If the liquid is further heated it

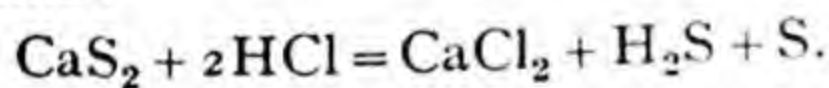
\* Hence it is not correct to say that 'plastic sulphur is formed by suddenly cooling *melted* sulphur': *boiling* sulphur is generally meant.



gradually darkens in colour: it becomes deep orange red, but it remains mobile until the temperature reaches about  $180^{\circ}$ , when the liquid *suddenly* thickens, so that the tube may be inverted without the sulphur running out. As the heating is continued, the sulphur becomes very dark-coloured, almost black, but the liquid becomes more mobile, and at the boiling point,  $444^{\circ}$ , it may be poured out into cold water. It then forms soft, rubber-like, transparent, yellow threads, called plastic sulphur (Fig. 230). These can be stretched easily and are somewhat elastic.

Plastic sulphur has a density of 1.92. It is insoluble in carbon disulphide. On standing for a few days the threads become opaque, hard and brittle, and lemon-yellow in colour; they then consist principally of  $\alpha$ -sulphur, although part is still insoluble in carbon disulphide.

**Milk of sulphur**, which is another amorphous form of sulphur, is precipitated as a fine white powder by adding an acid to a solution of a *polysulphide*, *i.e.*, one containing more sulphur than the normal sulphide, such as the yellow solution of calcium disulphide obtained by boiling sulphur with milk of lime:



The solution of calcium disulphide was called *thion hudor* (the 'divine,' or 'sulphurous, water') by the Greek chemists (p. 67).

**Uses of sulphur.**—Crude sulphur is used for making sulphur dioxide (and thence sulphuric acid) by burning it in air, and in the manufacture of carbon disulphide (p. 453). Refined sulphur is used in medicine, in the form of powder as a fungicide, and in the preparation of gunpowder, matches, fireworks, and dyes. Sulphur is also used in large quantities for *vulcanising rubber* (Chapter XXVIII).

Very large quantities of sulphur are used in preparing *bisulphite* solutions,  $\text{Ca}(\text{HSO}_3)_2$ , for use in the paper industry. It



FIG. 230.—PLASTIC SULPHUR.  
(By courtesy of D. van Nostrand Co.)

is estimated that over 180,000 tons of sulphur are used for this purpose annually, every ton of paper pulp produced requiring 280 lb. of sulphur. Bisulphites are also largely used as anti-septics. The next largest use is probably for dusting vines (100,000 tons per annum in Europe) to prevent the growth of fungus, and considerable amounts are also used in dusting hops to prevent the growth of mould. Fused sulphur has been used in America for impregnating railway sleepers.

**Hydrogen sulphide.**—Small amounts of hydrogen sulphide,

$H_2S$ , are formed by the decay of animal matter containing sulphur, and the unpleasant smell of rotten eggs is in part due to this gas. It occurs in sewer gas and in some kinds of natural gas. The atmosphere usually contains traces of it, which cause silver objects to tarnish, owing to the formation of a film of black silver sulphide,  $Ag_2S$ . Hydrogen sulphide is found in some mineral waters, *e.g.*, Harrogate water.

Hydrogen sulphide, sometimes called *sulphuretted hydrogen*, is produced in small amounts when hydrogen is passed over boiling sulphur, but the reaction is reversible and hydrogen sulphide

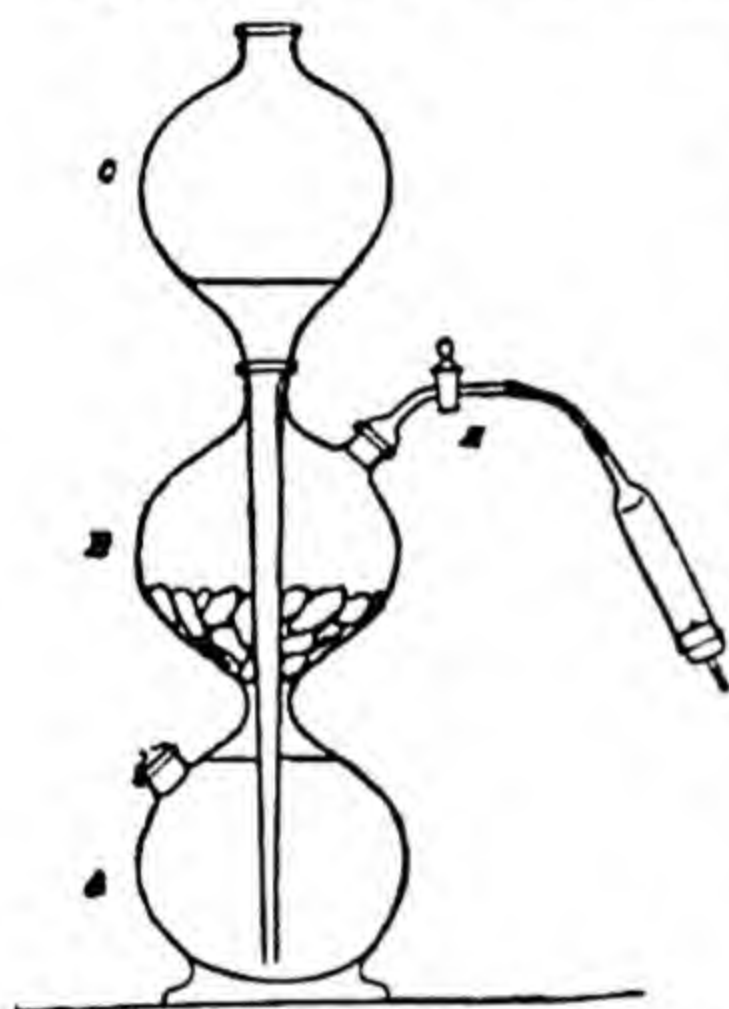
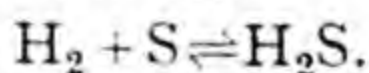
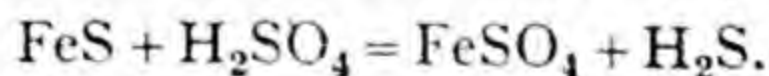


FIG. 231.—KIPP'S APPARATUS.

is largely decomposed on heating :



Hydrogen sulphide is usually *prepared* by the action of dilute sulphuric or hydrochloric acid on ferrous sulphide :

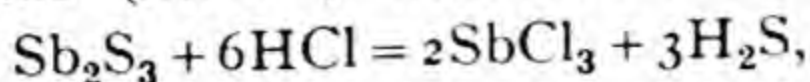


The reaction is carried out in a Kipp's apparatus (Fig. 231), so that the supply of the gas, which has a most unpleasant odour, may be interrupted at will. On account of the invariable presence of free iron in the ferrous sulphide, the gas so prepared contains hydrogen, which, however, does not interfere with its use in qualitative analysis. (*Iron pyrites*,  $FeS_2$ , is quite insoluble in dilute hydrochloric and sulphuric acids.)

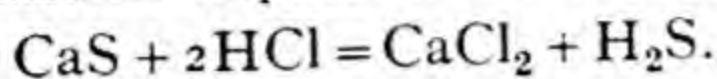
Hydrogen sulphide free from hydrogen is prepared by heating



antimony sulphide (*stibnite*) with concentrated hydrochloric acid :

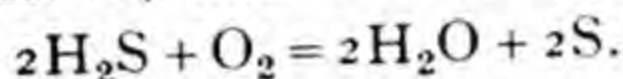


or by dissolving calcium sulphide in dilute hydrochloric acid :



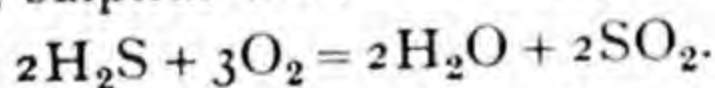
The gas may be collected over hot water (it is appreciably soluble in cold) or by downward displacement. It may be dried by calcium chloride.

**Properties of hydrogen sulphide.**—Hydrogen sulphide is a colourless gas with a powerful unpleasant odour, producing asphyxia or, in small quantities, headache and sickness. The solution in water, which is a weak acid, is easily oxidised in air, sulphur being deposited, and a little sulphuric acid is also formed :



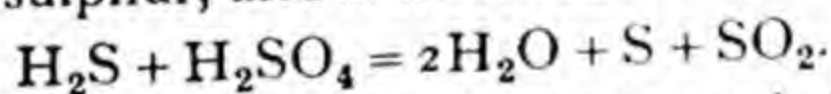
The addition of glycerin to the solution retards the oxidation.

The gas burns in air or oxygen with a blue flame, and owing to the high temperature it is dissociated in the interior of the flame ; the latter deposits sulphur on a cold porcelain dish. If the gas in a glass cylinder is ignited at the mouth, a deposit of sulphur is formed on the inside of the jar, owing to the deficiency of oxygen :  $2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S}$ . With a plentiful supply of oxygen, sulphur dioxide is formed :



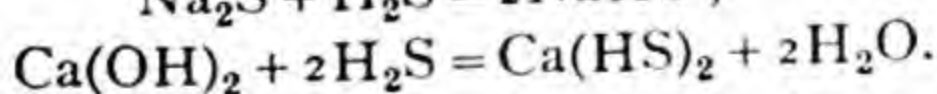
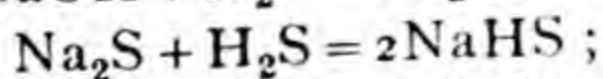
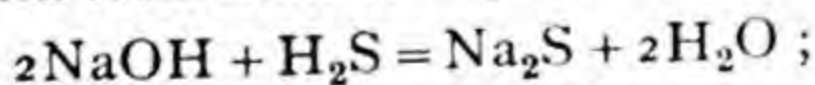
A mixture of 2 volumes of hydrogen sulphide and 3 volumes of oxygen explodes violently on ignition.

Concentrated sulphuric acid oxidises hydrogen sulphide, with precipitation of sulphur, and is itself reduced to sulphur dioxide :

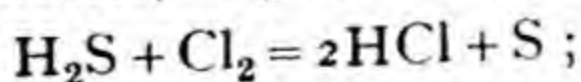


The gas ignites in contact with fuming nitric acid ; dilute nitric acid decomposes it with formation of sulphur, sulphuric acid and nitric oxide.

Hydrogen sulphide is absorbed by solutions of alkalies or by slaked lime, with formation of **sulphides** :



Hydrogen sulphide is oxidised when passed into chlorine water, or over bleaching powder, sulphur being deposited :



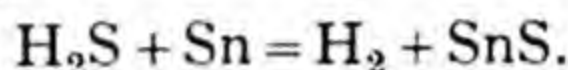
with a large excess of chlorine water, some sulphuric acid is formed :

$$\text{S} + 4\text{H}_2\text{O} + 3\text{Cl}_2 = \text{H}_2\text{SO}_4 + 6\text{HCl}.$$

Hydrogen sulphide is therefore a reducing agent.

The gas, or its solution (*e.g.*, mineral waters), may be detected by the black coloration, due to lead sulphide,  $\text{PbS}$ , produced with lead acetate. If alkali sulphides are present, they give a purple colour with a freshly prepared solution of sodium nitroprusside; this is not produced by free hydrogen sulphide.

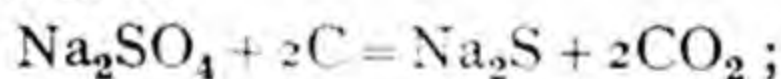
The composition of hydrogen sulphide is determined by heating tin or lead in a measured volume of the gas. It is decomposed, producing a sulphide of the metal and *an equal volume* of hydrogen :



Its density is 17,  $\therefore$  mol wt. = 34. Of this, the hydrogen  $\text{H}_2$  accounts for 2,  $\therefore$  wt. of  $\text{S} = 32$ , which is the atomic weight; hence the formula of hydrogen sulphide is  $\text{H}_2\text{S}$ .

**Sulphides.**—**Sodium sulphide**,  $\text{Na}_2\text{S}$ , is formed by dividing a solution of caustic soda into two halves, saturating one with hydrogen sulphide, when **sodium hydrogen sulphide**,  $\text{NaHS}$ , is formed, then adding the other portion of caustic soda, evaporating and crystallising as  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .

Sodium and calcium sulphides are formed by heating the sulphates with carbon :



Hydrogen sulphide precipitates sulphides of many metals from solutions of salts of the latter. These sulphides often have characteristic colours, so that the gas is used as a reagent in qualitative analysis. Many sulphides are precipitated from solutions acidified with hydrochloric acid: copper, lead, mercuric and bismuth salts, all give black sulphides,  $\text{CuS}$ ,  $\text{PbS}$ ,  $\text{HgS}$  and  $\text{Bi}_2\text{S}_3$  (brownish-black); cadmium and arsenic give yellow sulphides,  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ; antimony gives an orange-red sulphide,  $\text{Sb}_2\text{S}_3$ ; tin (stannous) a brown sulphide,  $\text{SnS}$ .

In some cases metals are precipitated only in *alkaline* solutions. An alkali sulphide, *e.g.*, ammonium sulphide, may be used. In this way zinc salts give a white precipitate of  $\text{ZnS}$ ; manganese gives flesh-coloured (sometimes greenish)  $\text{MnS}$ ; nickel, cobalt, and iron give black precipitates of  $\text{NiS}$ ,  $\text{CoS}$ , and  $\text{FeS}$ . The gas is used on the large scale to free sulphuric acid from dissolved arsenic trioxide: this is precipitated as sulphide.



Sulphides are also formed by direct combination of the elements. A mixture of iron filings and sulphur glows when heated, and ferrous sulphide,  $\text{FeS}$ , is produced. Copper turnings heated in a flask with a little sulphur become incandescent, cuprous sulphide,  $\text{Cu}_2\text{S}$ , being formed. Mercury and sulphur combine when triturated in a mortar, forming mercuric sulphide,  $\text{HgS}$ , which when so prepared is black.

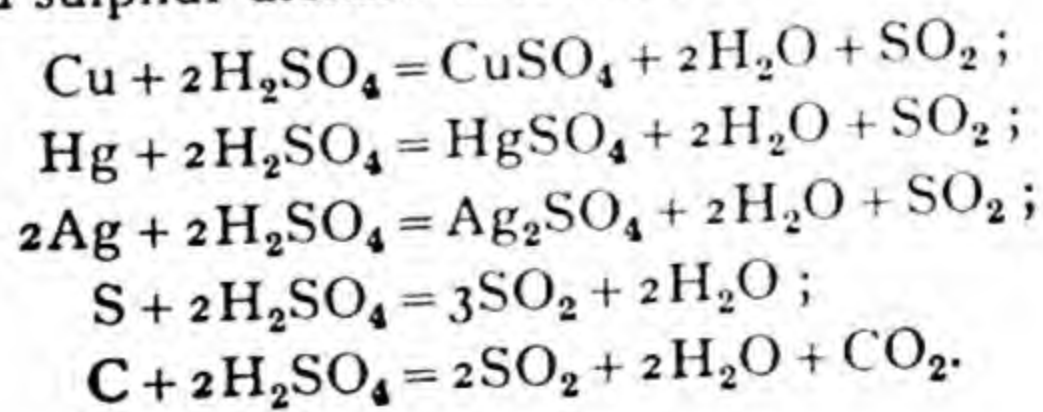
**\*Hydrogen persulphides.**—If *thion hudor* (p. 347) is added to an acid, instead of the reverse, as when milk of sulphur is prepared, and the liquid is kept well stirred, a yellow oil separates which contains two persulphides of hydrogen,  $\text{H}_2\text{S}_2$  (*cf.*  $\text{H}_2\text{O}_2$ ), and  $\text{H}_2\text{S}_3$ .

**Oxygen compounds of sulphur.**—When sulphur burns in air it forms a gaseous oxide, sulphur dioxide,  $\text{SO}_2$ , which has the well-known choking smell of burning sulphur. Further oxidation, in presence of water, gives sulphuric acid (*oil of vitriol*),  $\text{H}_2\text{SO}_4$ . Several compounds of oxygen with sulphur, and several oxyacids of sulphur, are known. The most important compounds, which we shall study in this chapter, are the following: Sulphur dioxide,  $\text{SO}_2$ , the anhydride of sulphurous acid,  $\text{H}_2\text{SO}_3$ ; sulphur trioxide,  $\text{SO}_3$ , the anhydride of sulphuric acid,  $\text{H}_2\text{SO}_4$ ; thiosulphuric acid,  $\text{H}_2\text{S}_2\text{O}_3$ , known only in salts, *e.g.*  $\text{Na}_2\text{S}_2\text{O}_3$ .

## SULPHUR DIOXIDE AND SULPHUROUS ACID

Homer (900 B.C.) refers to the use of burning sulphur in fumigation, and Pliny states that the fumes were also used for purifying cloth (*i.e.*, bleaching). Priestley (1774) obtained the pure gas by heating concentrated sulphuric acid with mercury, and collected it over mercury. He called it *vitriolic acid air*. Its composition was ascertained by Lavoisier in 1777; it is sulphur dioxide,  $\text{SO}_2$ .

**Preparation of sulphur dioxide.**—If concentrated sulphuric acid is heated with copper, mercury, silver, sulphur, or charcoal, it is reduced, and sulphur dioxide is formed:



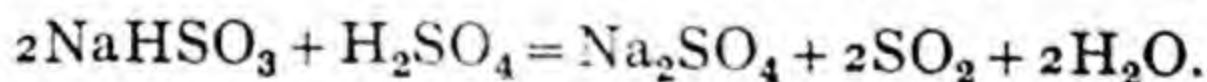
In the laboratory copper turnings are heated with concentrated sulphuric acid in a flask fitted with a thistle funnel (Fig. 232). The mixture becomes very dark, and gas is evolved with effervescence. When this occurs the flame is lowered or removed. The gas is collected by downward displacement or



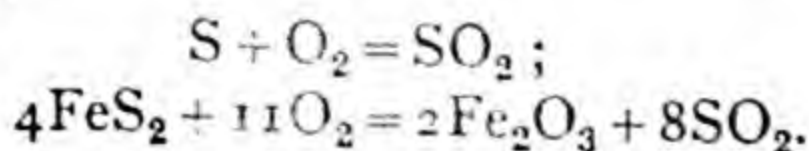
FIG. 232.—PREPARATION OF SULPHUR DIOXIDE BY HEATING COPPER WITH CONCENTRATED SULPHURIC ACID.

over mercury: it may be dried by passing through concentrated sulphuric acid. The reaction which takes place is really rather complicated: it is considered in Chapter XXXIV.

Sulphur dioxide is also obtained by dropping concentrated sulphuric acid into a solution of sodium hydrogen sulphite:



Sulphur dioxide (*mixed with atmospheric nitrogen*) is made on the large scale by burning sulphur or iron pyrites in air in special burners:



**Properties of sulphur dioxide.**—Sulphur dioxide is a colourless, heavy gas with a choking smell. It is poisonous, even when



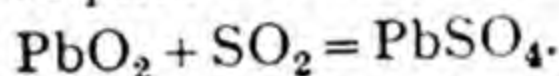
diluted with 2500 volumes of air, and attacks the eyes. Sulphur dioxide has antiseptic properties and is used in fumigation and in preserving fruit: it is very injurious to vegetation. It is freely soluble in water, forming an acid solution no doubt containing sulphurous acid,  $\text{H}_2\text{SO}_3$ , of which it is the anhydride. The acid is unknown in the pure state: it is unstable, and on boiling the solution all the sulphur dioxide is expelled.

Sulphur dioxide is easily liquefied by pressure or by cooling in a spiral tube immersed in ice and salt. The liquid is a commercial article and is sold in glass siphons (Fig. 233), or (on the large scale) in steel tanks holding up to 10 tons. On evaporation, cold is produced and liquid sulphur dioxide is used in some types of domestic refrigerators.

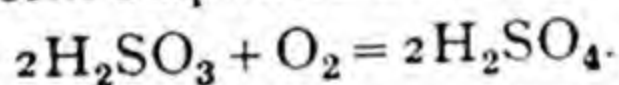


FIG. 233.—LIQUID SULPHUR DIOXIDE.

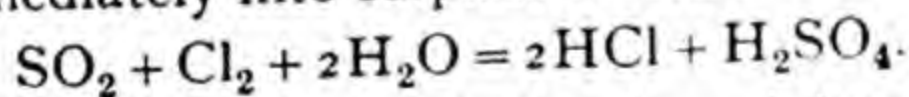
Sulphur dioxide does not support the combustion of a taper, but heated potassium and tin burn in the gas, and heated lead peroxide in a deflagrating spoon glows when lowered into a jar of sulphur dioxide, white lead sulphate being produced:



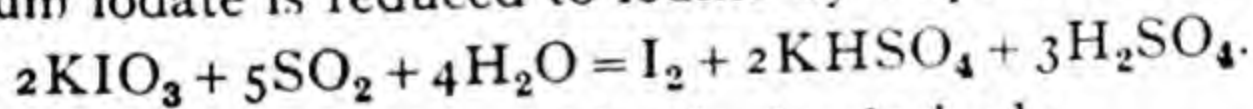
A solution of sulphur dioxide slowly takes up oxygen on exposure to air to form sulphuric acid:



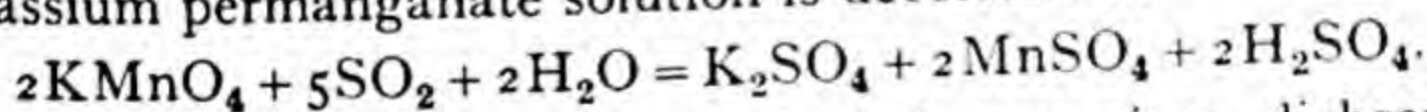
It acts as a reducing agent. Chlorine, bromine and iodine convert it immediately into sulphuric acid:



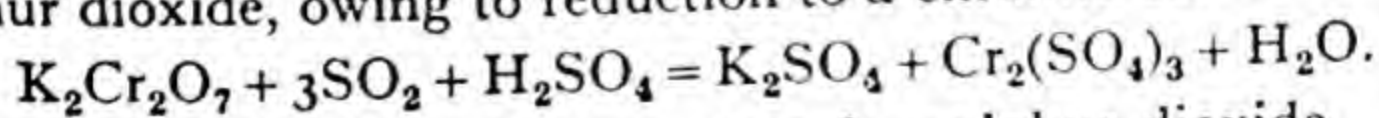
Potassium iodate is reduced to iodine by sulphur dioxide:



Potassium permanganate solution is decolorised:

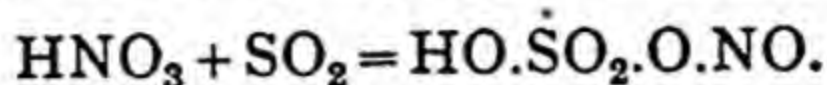


A piece of paper dipped in acidified potassium dichromate solution is changed from yellow to green when exposed to sulphur dioxide, owing to reduction to a chromic salt:



The last reaction is used as a test for sulphur dioxide. The smell of the gas is also very characteristic.

When passed into concentrated nitric acid, sulphur dioxide forms a mass of *chamber crystals* or nitroso-sulphuric acid (p. 359) :



Dilute nitric acid *slowly* oxidises sulphur dioxide to sulphuric acid.

Sulphur dioxide as such is used in refrigeration, in bleaching wool and straw, in refining and bleaching sugar, in softening hides in tanning, as an antiseptic and for fumigation, and the liquid has been used in the purification of petroleum. Its salts are used on a very large scale in making paper pulp. The bleaching action is due to reduction or to the formation of colourless compounds.



FIG. 234.—THE VOLUMETRIC COMPOSITION OF SULPHUR DIOXIDE.

The composition of sulphur dioxide is determined as follows. A *small* piece of sulphur lying in a metal spoon is ignited in dry oxygen gas confined over *dry* mercury in the apparatus shown in Fig. 234, by means of a piece of fine platinum wire heated electrically in contact with the sulphur. When the apparatus is cool it is found that the mercury levels are practically unchanged, *i.e.*, *sulphur dioxide contains its own volume of oxygen*.

The vapour density of sulphur dioxide is 32, hence its molecular weight is 64. The molecule contains a molecule, or 32 parts, of oxygen, and therefore  $64 - 32 = 32$  parts, or one atom, of sulphur. Hence the formula of the gas is  $\text{SO}_2$ .

**Sulphites.**—The hypothetical sulphurous acid,  $\text{H}_2\text{SO}_3$ , is a dibasic acid and forms two series of salts :

#### ACID SULPHITES.

sodium hydrogen sulphite,  $\text{NaHSO}_3$ ,

calcium hydrogen sulphite,  $\text{Ca}(\text{HSO}_3)_2$ ,

#### NORMAL SULPHITES.

sodium sulphite,  $\text{Na}_2\text{SO}_3$ ;

calcium sulphite,  $\text{CaSO}_3$ .

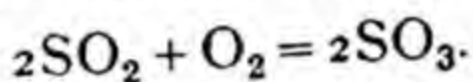
When a solution of caustic soda is divided into two equal parts and one is saturated with sulphur dioxide, a solution of sodium hydrogen sulphite (often called 'sodium bisulphite') is formed. If the other portion of caustic soda is added to this solution, and the liquid evaporated, crystals of normal sodium



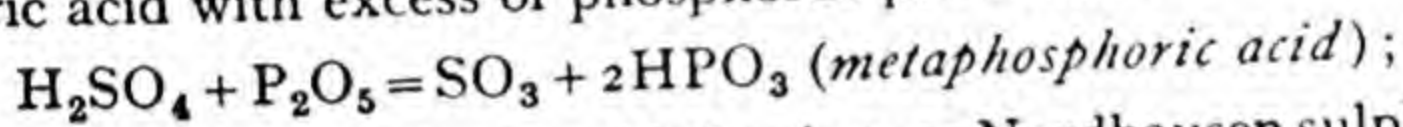
sulphite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , are formed. Sodium metabisulphite (*sodium pyrosulphite*),  $\text{Na}_2\text{S}_2\text{O}_5$ , is used in photography. When passed into a large volume of lime water, sulphur dioxide gives a white precipitate of calcium sulphite,  $\text{CaSO}_3$ , soluble to a clear solution of calcium bisulphite,  $\text{Ca}(\text{HSO}_3)_2$ , when excess of the gas is passed in (*cf.*  $\text{CO}_2$ , p. 299). Sulphites give with barium chloride a white precipitate of  $\text{BaSO}_3$ , which is *soluble in hydrochloric acid*.

### SULPHUR TRIOXIDE.

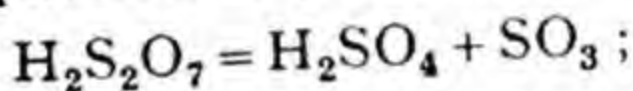
**Sulphur trioxide.**—Sulphur trioxide, or *sulphuric anhydride*,  $\text{SO}_3$ , is usually prepared by passing a dry mixture of sulphur dioxide and oxygen over heated platinised asbestos (a catalyst) in a glass tube and collecting the trioxide in a dry receiver cooled in a freezing mixture :



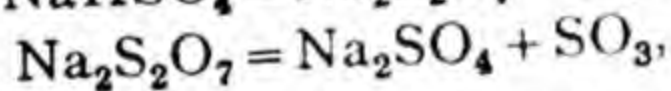
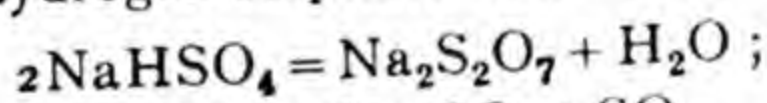
Sulphur trioxide is also obtained by distilling concentrated sulphuric acid with excess of phosphorus pentoxide :



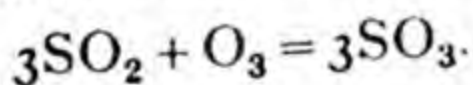
by distilling pyrosulphuric acid (fuming, or Nordhausen sulphuric acid, or oleum) :



by strongly heating sodium pyrosulphate, which is formed by heating sodium hydrogen sulphate at  $300^\circ$  :



or by the direct combination of sulphur dioxide and ozone :



This is one of the very few cases in which the ozone molecule as a whole takes part in oxidation.

Sulphur trioxide is a colourless crystalline solid which has an intense attraction for water. It dissolves almost explosively in water, with the evolution of much heat, forming sulphuric acid, but dissolves quietly in concentrated sulphuric acid, forming fuming sulphuric acid (or 'oleum'). On exposure to moist air the trioxide, or fuming sulphuric acid, emits dense white fumes, composed of droplets of sulphuric acid. The vapour of sulphur trioxide when passed through a red-hot tube

is decomposed into sulphur dioxide and oxygen, and its composition may be determined in this way :

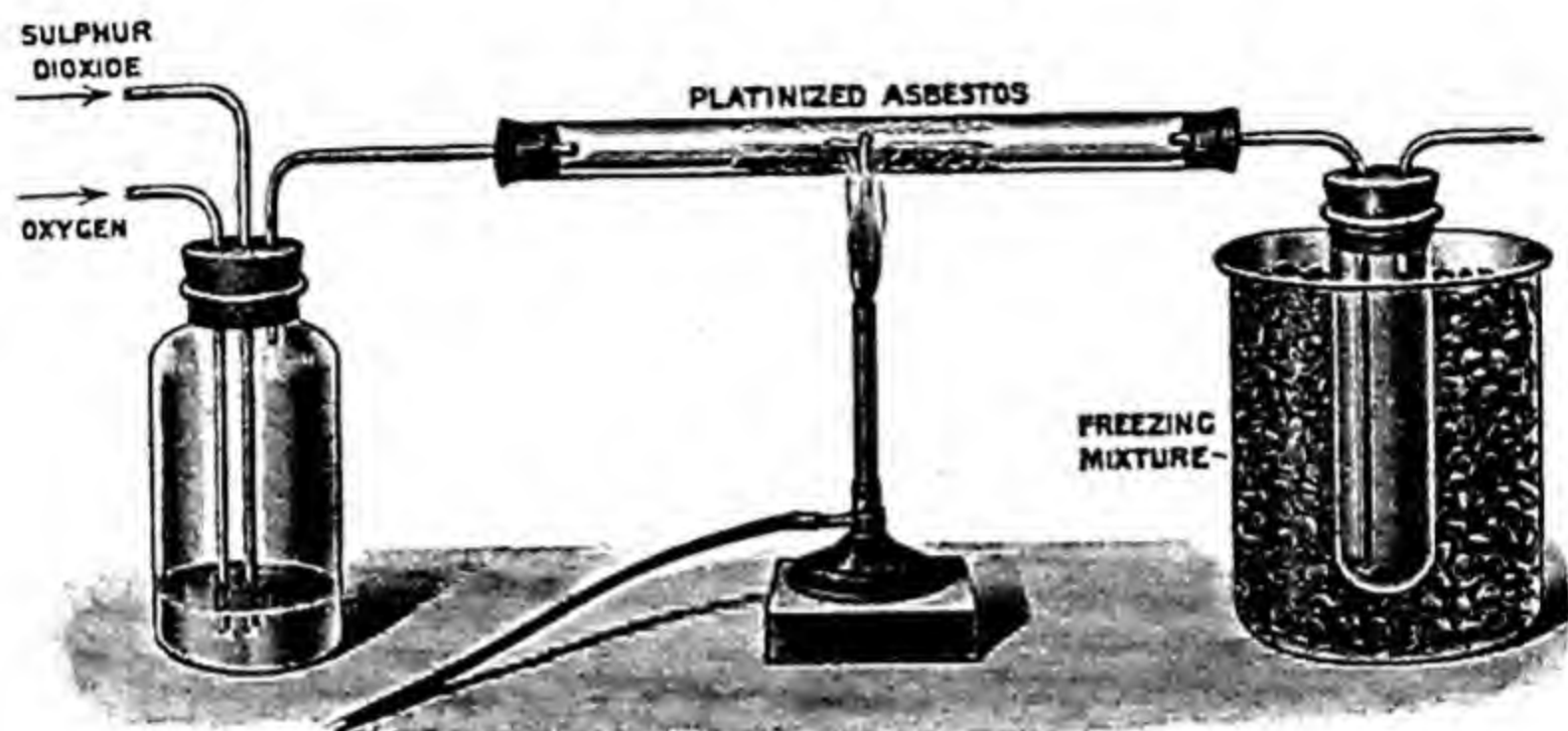
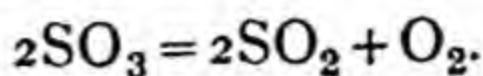
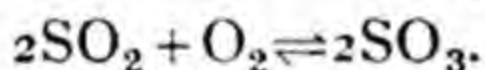


FIG. 235.—PREPARATION OF SULPHUR TRIOXIDE.

**The contact process for sulphuric acid.**—Sulphur dioxide mixed with nitrogen and oxygen is produced by burning sulphur or iron pyrites in excess of air. The gas so produced is carefully purified by cooling it and filtering it through coke wetted with concentrated sulphuric acid, and is then passed over heated platinum in a contact apparatus, when sulphur trioxide is formed :

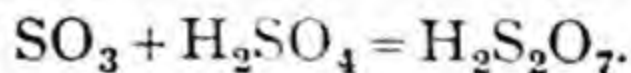


In presence of excess of oxygen the conversion is nearly complete (p. 222).

In the **Badische process** (Fig. 236) the purified gas is passed into an iron cylinder with inlet and outlet pipes, fitted inside with vertical iron tubes packed with platinised asbestos. By letting the incoming gas sweep over the outside of the hot tubes in which the reaction occurs, no further external heating is needed when once the reaction has been started, since a considerable amount of heat is evolved, and the process goes on continuously.

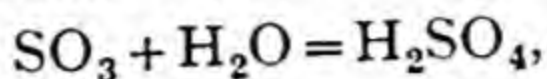
The complete purity of the gas passing to the converters is essential, otherwise the platinum ceases to act catalytically, or is 'poisoned.'

The sulphur trioxide is *not* passed into water, since then an unmanageable fog of droplets of acid is formed, but is absorbed by concentrated sulphuric acid, producing oleum :



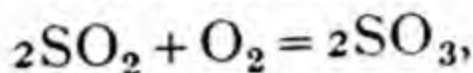


If ordinary concentrated sulphuric acid is required, water is added continuously as the trioxide is absorbed, the reaction :

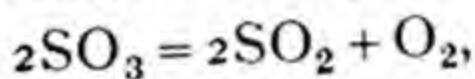


occurring quietly in the liquid acid. This process is used to produce oleum or very concentrated acid ; somewhat weaker acid is usually made by the chamber process (p. 359).

The action of the platinum catalyst in the manufacture of sulphur dioxide by the contact process is to increase the speed of the reaction :



which is exceedingly slow in its absence. A definite state of equilibrium is reached, since the sulphur trioxide is also decomposed by heat :



and this reverse reaction is also accelerated by the platinum catalyst. The resulting state of equilibrium is unaffected

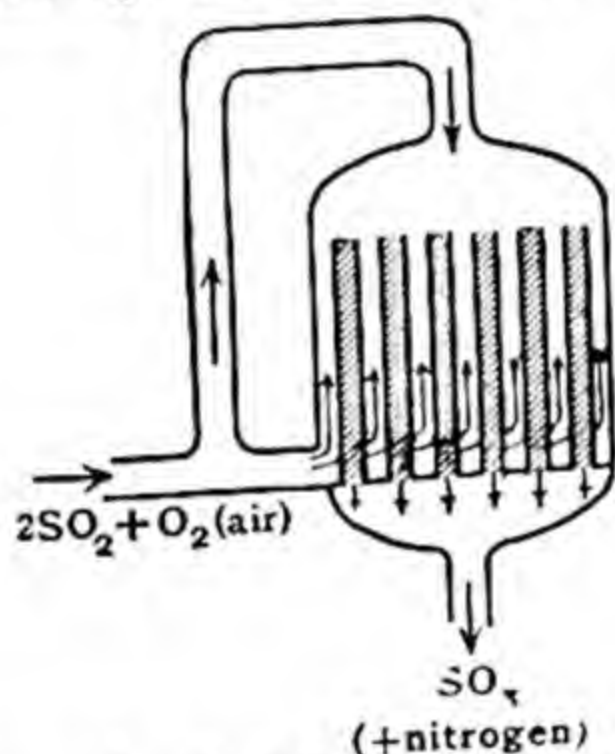


FIG. 236.—BADISCHE CONVERTER.

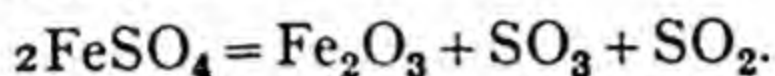
by the presence of the catalyst, which changes the speeds of both the direct and the reverse reactions to the same extent. *It is impossible to increase the yield in equilibrium by means of a catalyst* : what the catalyst does is to hasten very considerably the attainment of the equilibrium state.

Even in the presence of a catalyst, the rate of formation of sulphur trioxide is very small unless the temperature is raised. Since the higher temperatures cause decomposition of sulphur trioxide, as low a temperature as possible is used, but it must be high enough to produce a reasonably rapid conversion of sulphur dioxide into trioxide. In practice a balance is struck at a temperature of about  $450^\circ$  and in presence of excess of

oxygen the action of mass (p. 222) causes almost complete oxidation of the sulphur dioxide.

### SULPHURIC ACID.

**\*History of sulphuric acid.**—Sulphuric acid is described by the mediaeval alchemists, who obtained it by distilling ferrous sulphate (*green vitriol*) and called it oil of *vitriol* :



The vapour of sulphur trioxide was dissolved in water (Fig. 237).

In 1666 Le Febure obtained the acid by burning sulphur in presence of moisture (Fig. 238); Lemery in 1675 made it by

deflagrating a mixture of sulphur and nitre over a dish of water under a glass bell, and a small works using this process was established in 1740 by Ward, at Richmond. The acid obtained was called oil of vitriol *per campanum*. Roebuck, in 1746, at Prestonpans, replaced the fragile glass vessels by lead chambers 6 ft. wide, and these were enlarged in later works. These chambers were introduced into France in 1766 by the Englishman Holker, and in 1774 La Follie employed a jet of steam in the chamber. A considerable advance was possible after the researches of Clement and Desormes (1793),\* who pointed out the importance of a current of air in the chambers, and in 1806 these



FIG. 237.—PREPARATION OF OIL OF VITRIOL BY GLAUBER (1648), BY DISTILLING FERROUS SULPHATE.

chemists gave a correct interpretation of the reactions occurring in the chambers, particularly the part played by the oxides of nitrogen. A continuous process, in which the sulphur dioxide was produced from sulphur in separate burners, and admitted, together with nitrous fumes, air, and steam, to the chambers,

\* C. B. Desormes (1777-1862) and Clement-Desormes, *d.* 1841.



was introduced by Holker into the French works of Chaptal in 1810. The use of pyrites as a source of sulphur dioxide, introduced by Hill, of Deptford, in 1818, and the invention of the Gay-Lussac and Glover towers (p. 361) in 1827 and 1859, respectively, led to the modern chamber acid industry.

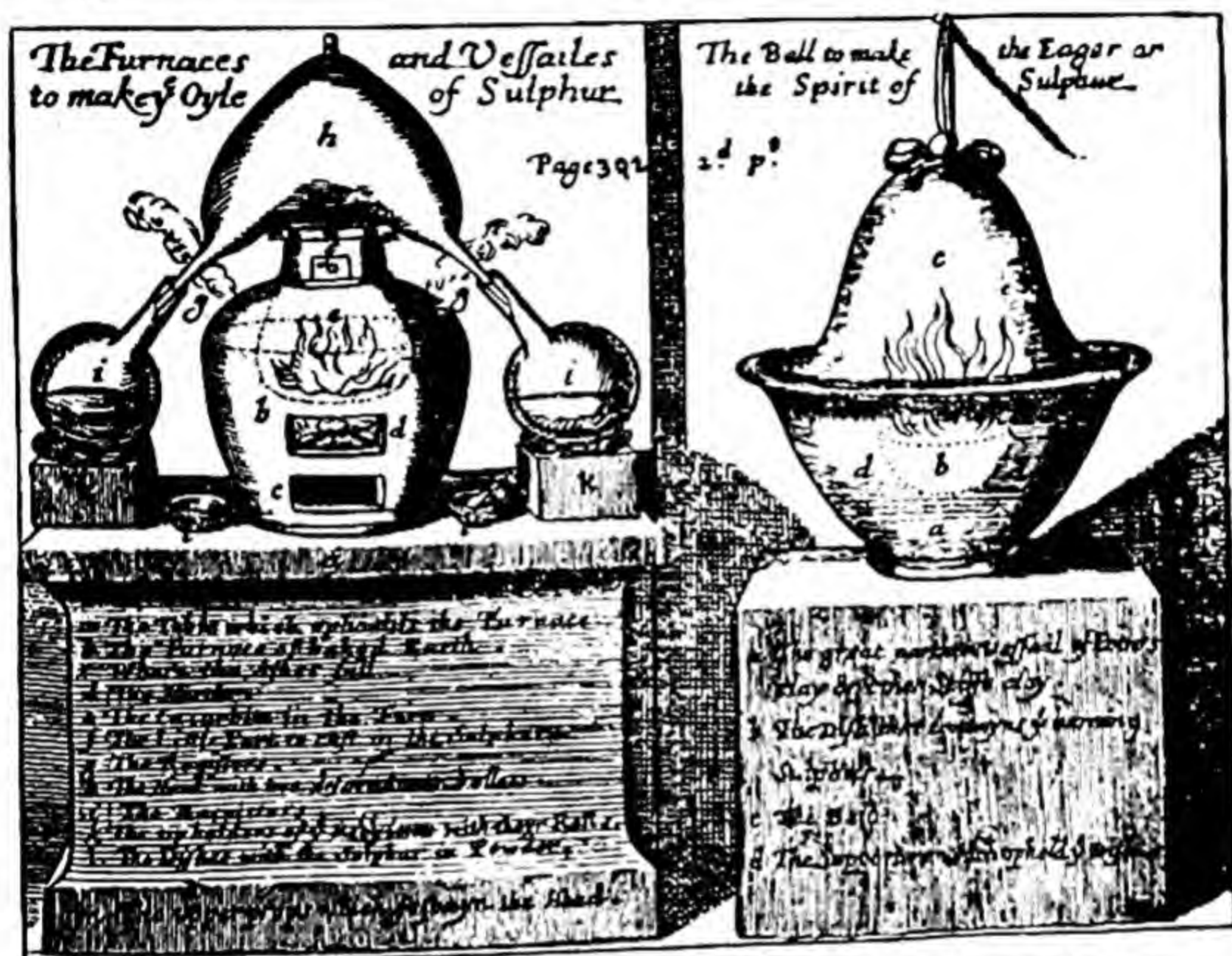


FIG. 238.—PREPARATION OF SULPHURIC ACID (OIL OR SPIRIT OF SULPHUR) ACCORDING TO LE FEBVRE (1066).

More than one million tons of sulphuric acid are produced annually by *each* of the three countries, Great Britain, Germany, and America.

**The chamber process.**—The reactions in the sulphuric acid chambers occur between *sulphur dioxide*, *oxygen*, *water*, and *oxides of nitrogen*. The oxides of nitrogen act catalytically; in all probability an intermediate compound, called 'chamber crystals' (nitroso-sulphuric acid,  $\text{HO} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{NO}$ ), is alternately formed and decomposed by water into sulphuric acid and oxides of nitrogen, which react again.

The chamber reactions are illustrated by the following experiment. A large flask, *A*, is fitted with four inlet tubes, as shown in

Fig. 239, and a small outlet tube. Three of the tubes are connected with wash-bottles containing concentrated sulphuric acid. One of these is connected with a siphon of liquid sulphur dioxide, one to a gas-holder containing oxygen, and the third to an apparatus for generating nitric oxide. The fourth tube is connected with a small flask, *B*, containing water, which may be heated, and through which oxygen may be bubbled. A rapid stream of oxygen is first passed through the apparatus. Nitric oxide is then passed in, which at once forms a red gas, nitrogen dioxide,  $\text{NO}_2$ . Sulphur dioxide is then passed in at the same

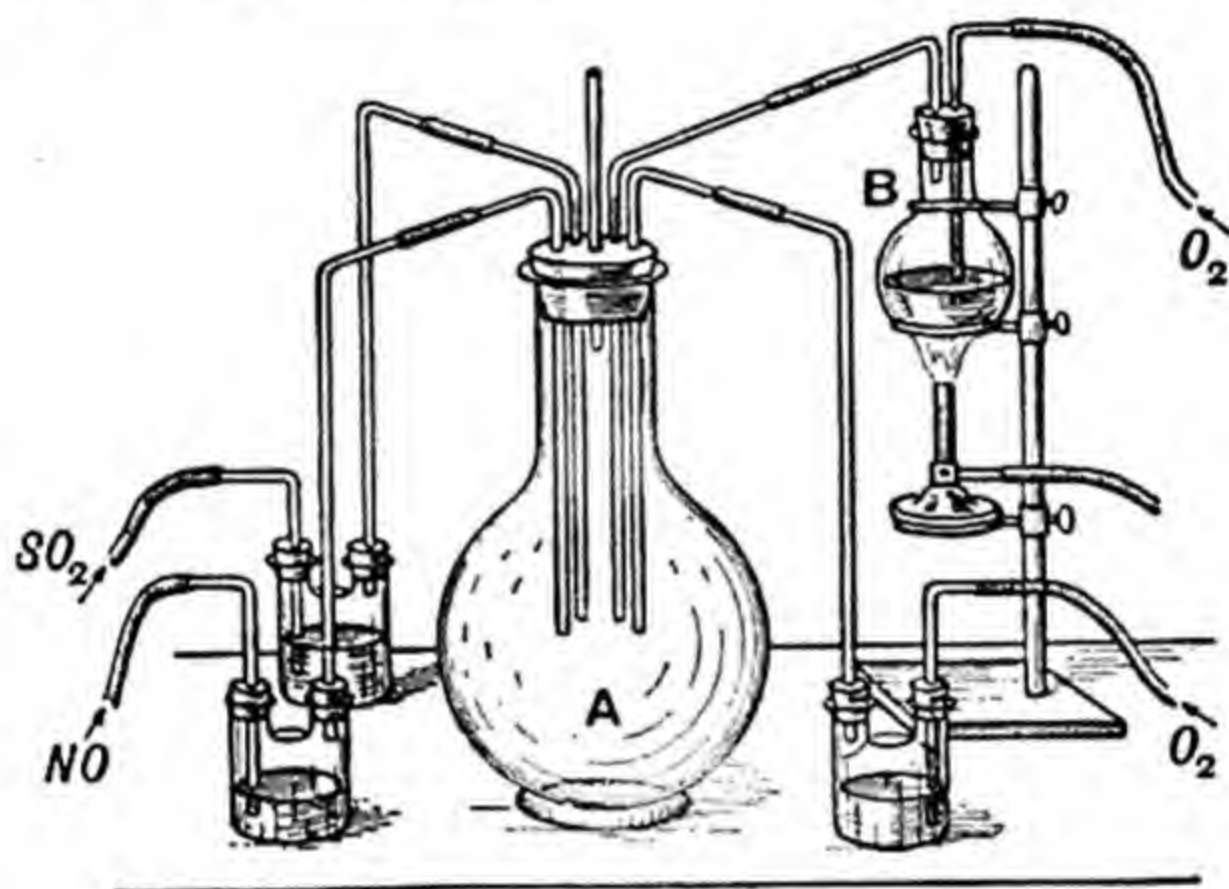
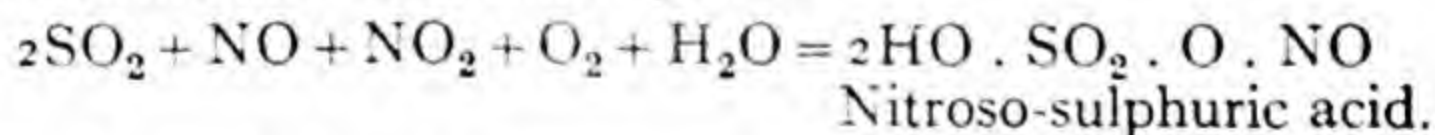
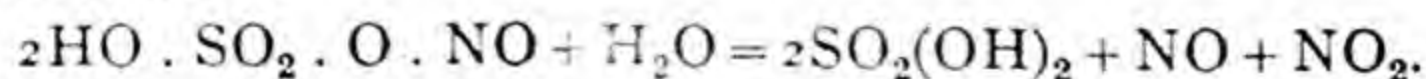


FIG. 239.—EXPERIMENT ILLUSTRATING THE MANUFACTURE OF SULPHURIC ACID BY THE CHAMBER PROCESS.

rate as the nitric oxide, and, after a short time, a current of oxygen is passed through the hot water in *B* to carry moisture into the globe. White star-shaped crystals of nitrososulphuric acid form on the inside of the flask. The colour of the gases at the same time becomes much paler :



The gases are next swept out by a rapid current of dry oxygen, and the water in the flask *B* is boiled. When the steam comes in contact with the chamber crystals they dissolve with effervescence, producing red fumes of oxides of nitrogen and sulphuric acid :

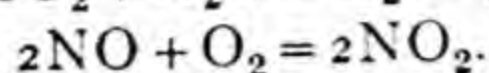
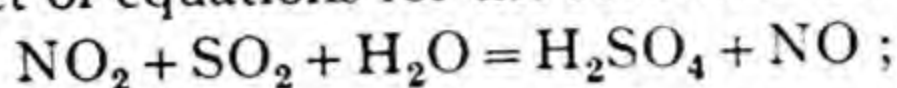


In the manufacturing process the steam (or water spray) is



added together with the other gases and chamber crystals are *not* formed as a separate stage, but are decomposed as fast as they are produced.

A simpler set of equations for the reactions is :



**Manufacture of sulphuric acid by the chamber process.**—Iron pyrites is burnt in furnaces, called **pyrites burners**, the supply of air being regulated by sliding doors. Rotary kilns, consisting of iron cylinders lined with firebrick, with a series of shelves so arranged that the ore is raked from shelf to shelf until the burnt ore is discharged at the bottom, are also used.

The burner gas passes to a **dust-catcher**, containing baffle-walls, and then through a **nitre-oven**, in which pots containing

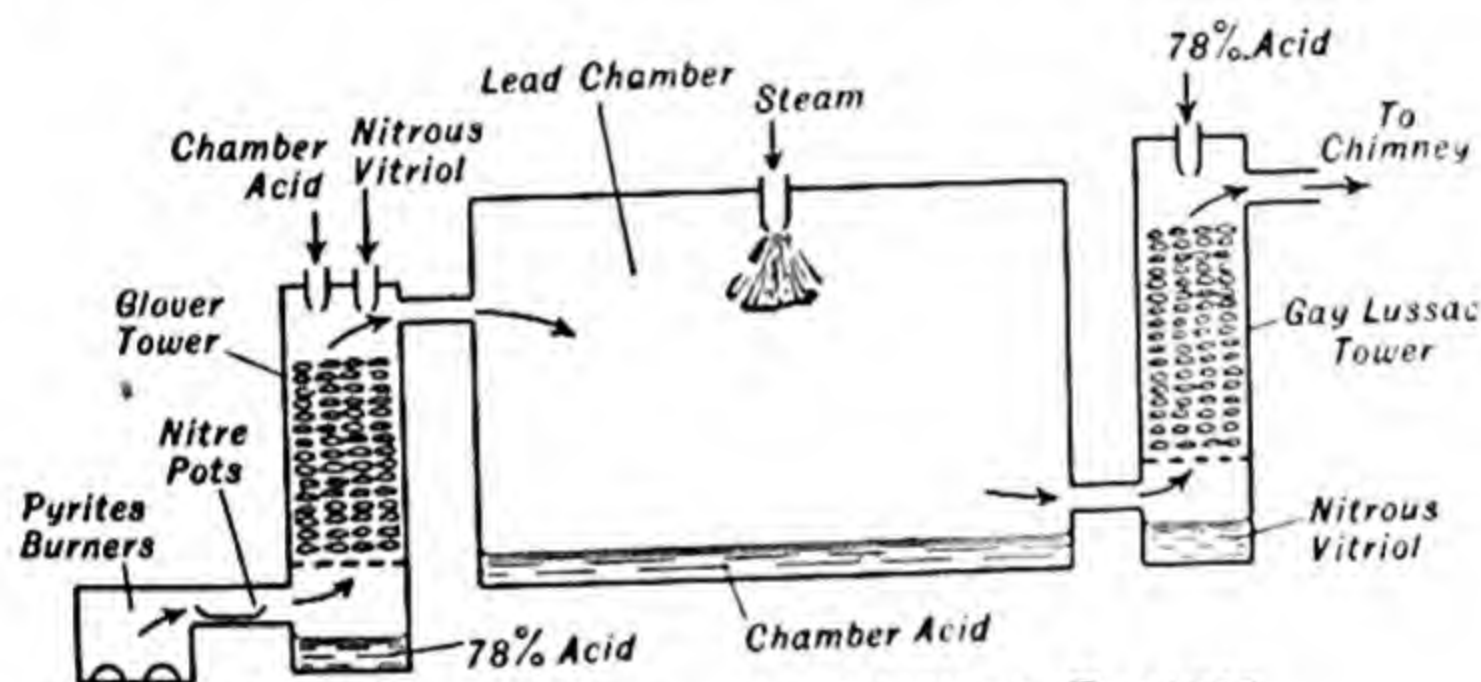


FIG. 240.—DIAGRAM OF CHAMBER PROCESS.

sodium nitrate and sulphuric acid are placed. These supply the oxides of nitrogen to make up losses from the plant. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia (p. 388). From the nitre oven the hot gases pass into the **Glover tower**, seen on the left in Fig. 240. This is a lead tower lined with acid-resisting bricks, packed with flints. Down this tower two streams of acid, from the tanks seen at the top, are passed. One stream consists of dilute acid (65-70 per cent.  $\text{H}_2\text{SO}_4$ ) from the lead chambers; the other consists of stronger acid (78 per cent.  $\text{H}_2\text{SO}_4$ ) containing oxides of nitrogen (in the form of nitrososulphuric acid) from the **Gay-Lussac tower** seen on the right. The functions of the Glover tower are three: (a) to cool the burner gases before they enter the chambers; (b) to denitrate the acid from the Gay-

Lussac tower, by dilution with chamber acid, and heating ; (c) to concentrate the weak acid to about 78 per cent.  $\text{H}_2\text{SO}_4$  for sale, or for use in the Gay-Lussac tower, and at the same time provide some steam for the chambers.

From the Glover tower the gases now pass, by a lead main, to the first of the set of lead chambers. These are formed of sheet lead, are oblong or sometimes drum-shaped, and dip into large lead saucers with a seal of acid.

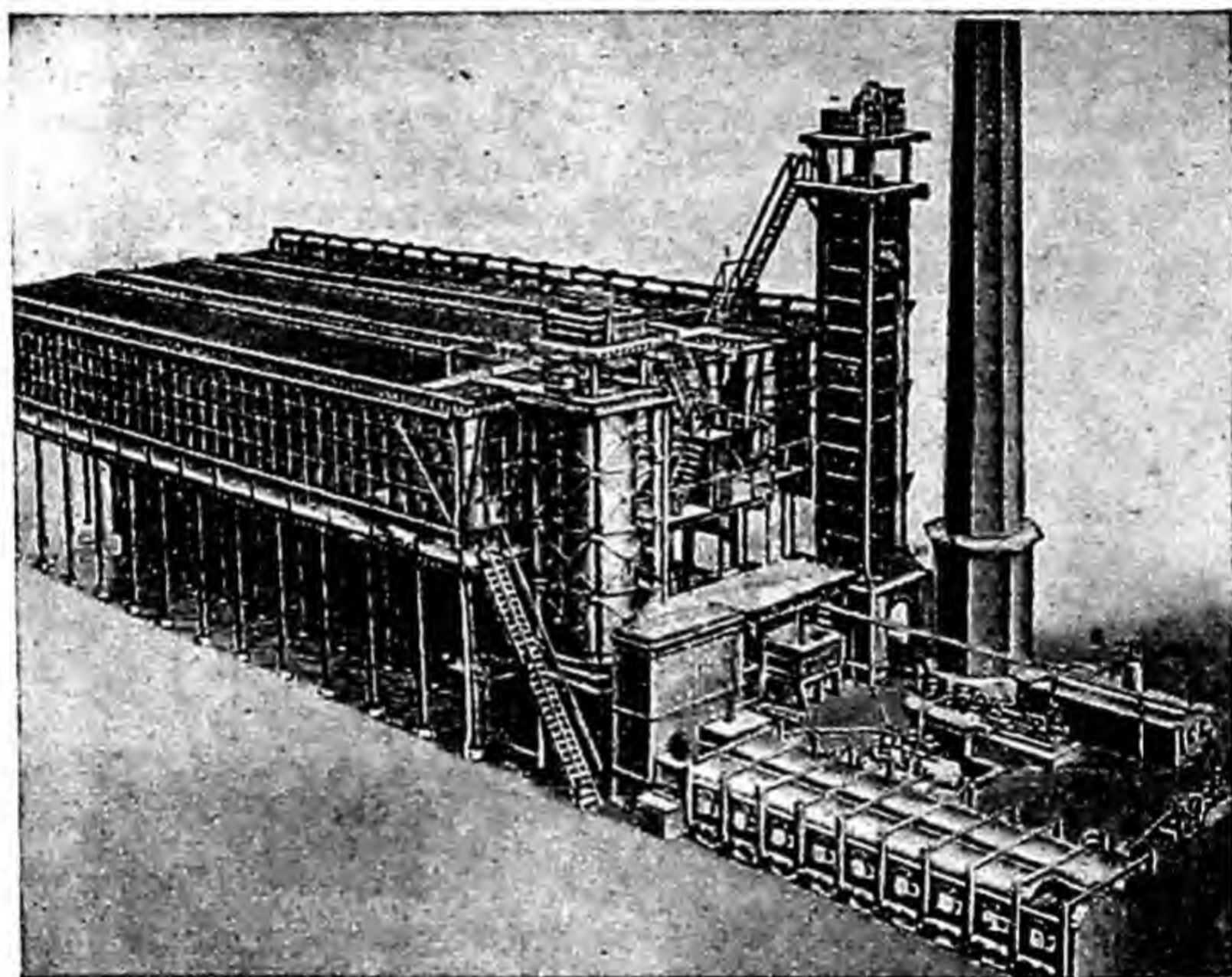


FIG. 241.—BIRD'S-EYE VIEW OF A SULPHURIC ACID CHAMBER PLANT.

Steam, or usually a fine spray of liquid water from several jets in the roof, is blown into the chamber. Sulphuric acid is produced in the form of a fog of small drops, which settle down into liquid **chamber acid** (65-70 per cent.  $\text{H}_2\text{SO}_4$ ) on the floor of the chamber.

The gases from the last chamber, containing the oxides of nitrogen in circulation through the plant, now pass to the Gay-Lussac tower, a lined lead tower, packed with hard coke, and fed with cold Glover acid (78 per cent.  $\text{H}_2\text{SO}_4$ ). Its function is to recover the oxides of nitrogen in the exit gases from the chambers. These are absorbed, producing **nitrous vitriol**,



containing nitrososulphuric acid, which is pumped to the Glover tower for denitration. The waste gas from the Gay-Lussac tower passes to a chimney, which maintains a draught through the whole system. Fig. 241 shows a bird's-eye view of a complete sulphuric acid chamber plant.

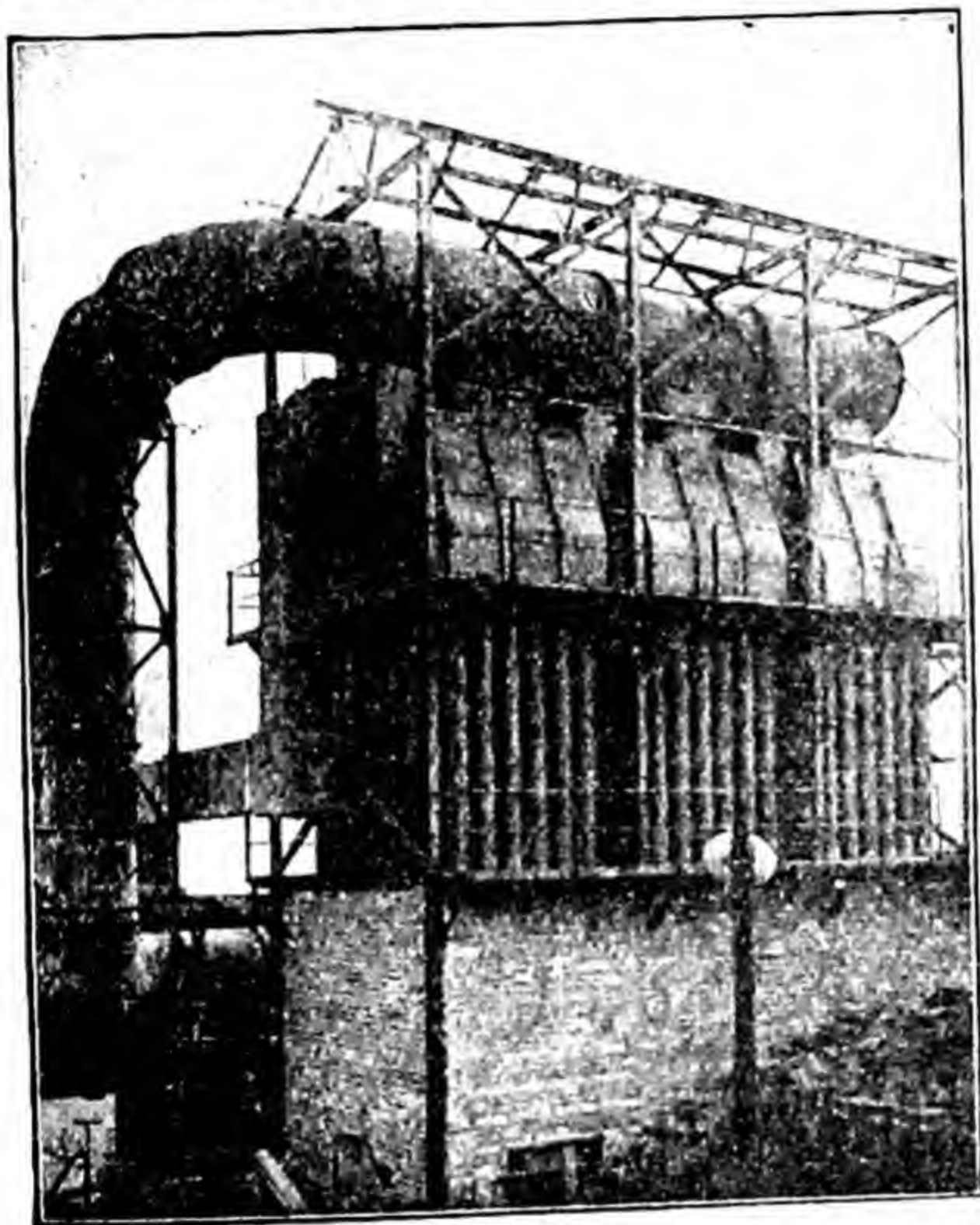


FIG. 242.—LODGE-COTTRELL PRECIPITATOR FOR TREATING THE GASES FROM LEAD BLAST FURNACES.

The acid is *concentrated* to about 95 per cent in various ways. In one process a spray of 78 per cent acid is sent down a brick tower (**Gaillard tower**) in which it meets hot gases ascending from a coke furnace. Vapours of very weak acid pass off, and the concentrated acid falls to the base of the tower, where it is collected. If this 95 per cent. acid is heated in iron pans, a 98 per cent. acid is obtained.

The acid fumes from the concentrators may be condensed by

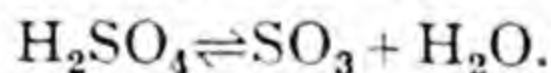
means of **electrostatic precipitation**. They are passed through a chamber in which lead pipes are hung, with lead covered bars hanging vertically between them. These are charged to a potential of 20,000 volts. The acid droplets are attracted to the plates, and the liquid deposited on the latter runs off to collecting tanks and is returned to the concentrators.

Electrostatic precipitation is also used in power stations to eliminate grit, in steelworks and cement works to separate dust from blast furnace and kiln gases, in depositing all kinds of metallurgical fumes, and in eliminating tar from coal gas, and all kinds of chemical acid mists and fumes.

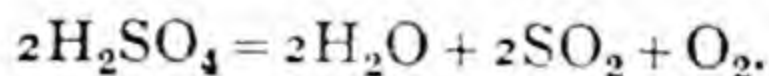
The installation shown in Fig. 242 is for separating dust from gases from lead-smelting furnaces. It consists of metal pipes with vertical electrodes inside. Continuous rapping gear dislodges the solid deposited on the electrodes, while hand-operated rapping hammers outside the pipes vibrate these occasionally to clear the dust deposited on the inside surfaces. The dust falls into large boxes. This dust had formerly to be cleaned out of large settling chambers, and some passed out of the chimney as smoke.

**Properties of sulphuric acid.**—Ordinary concentrated sulphuric acid (*oil of vitriol*) contains about 98 per cent. of  $\text{H}_2\text{SO}_4$ . It is a colourless, oily liquid, heavier than water. It has a very corrosive action on the skin and should be handled with great care. After pouring the liquid from a bottle, any drops which may run down the outside of the latter should be removed with a piece of waste rag, since they may get on the hands or on the bench, and in the second case the wood will be charred. The bottle is best kept standing in a shallow saucer on the shelf.

On heating, the liquid begins to emit fumes, and at its boiling point, which is rather high, dense white fumes are evolved, due to the *dissociation* of the acid into sulphur trioxide and water on heating, and the recombination of these substances in the cold air to form a dense fog of droplets of sulphuric acid (see p. 356) :



When very strongly heated, say by passing its vapour through a red hot tube, sulphuric acid is decomposed into sulphur dioxide, water, and oxygen :



These gases do *not* recombine to form sulphuric acid on cooling.

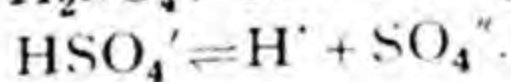
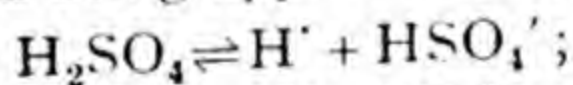


Concentrated sulphuric acid has a *strong affinity for water*. When the acid is mixed with water a considerable amount of heat is given out, and the liquid may boil. In practice, it is always safest to add the acid in a thin stream to the water, with stirring. *The water should never be added to the acid*. The diluted acid occupies a smaller volume than its constituents. If the acid is mixed with snow, cold is produced, because the latent heat of fusion of ice exceeds the heat evolved on mixing the acid with liquid water.

On account of its great affinity for water, concentrated sulphuric acid is used for drying gases on which it does not act chemically.

The affinity of sulphuric acid for water is also shown by the charring of organic matter containing carbon, hydrogen, and oxygen, by the acid. The elements of water are removed, and black carbon is left. For this reason the commercial acid is always brown. When concentrated sulphuric acid is added to a strong syrup of cane-sugar,  $C_{12}H_{22}O_{11}$ , contained in a beaker standing in a stoneware trough, the mixture rapidly becomes dark in colour and hot, and froths up into a black mass of finely-divided carbon, clouds of steam and sulphur dioxide being evolved.

In aqueous solution sulphuric acid behaves as a strong acid (p. 208), since it is largely ionised. The ionisation occurs in two stages, the second being appreciable only at high dilution:

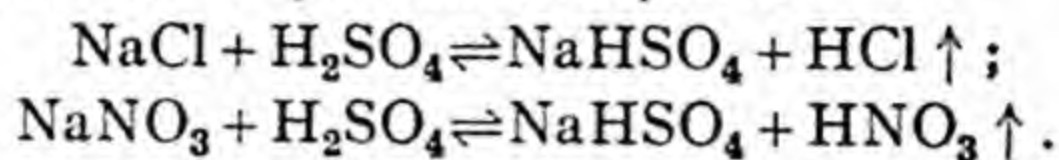


Two series of **sulphates** are therefore known, the acid and **normal salts**, corresponding with the formulae  $RHSO_4$  and  $R_2SO_4$ . Many of these sulphates are important minerals: *gypsum*,  $CaSO_4 \cdot 2H_2O$ ; *anhydrite*,  $CaSO_4$ ; *barytes*,  $BaSO_4$ ; *celestine*,  $SrSO_4$ ; *glauberite*,  $CaSO_4 \cdot Na_2SO_4$ ; and *kieserite*,  $MgSO_4 \cdot H_2O$ .

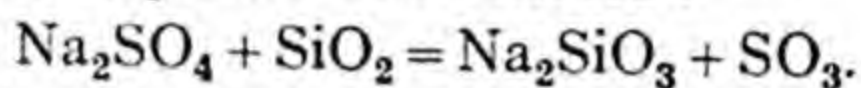
Most sulphates are crystalline, and soluble in water. The sulphates of lead, calcium, and strontium are sparingly soluble in water; barium sulphate is practically insoluble in water and dilute acids, and its formation as a white precipitate is used as a test for sulphuric acid or soluble sulphates. A solution of barium chloride is added to the liquid to be tested, and then *concentrated* hydrochloric acid. Care must be taken not to add *concentrated* hydrochloric acid to a solution along with barium chloride when testing for sulphates, since a precipitate of barium chloride, which is sparingly soluble in concentrated hydrochloric

acid, may then be formed. Salts of many other acids (phosphates, sulphites, etc.) give white precipitates with barium chloride, but not in presence of dilute hydrochloric acid.

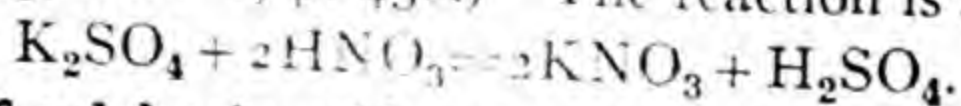
Sulphuric acid displaces nitric or hydrochloric acids when heated with nitrates or chlorides, since it is less volatile than these acids, which escape from the system:



In reality nitric and hydrochloric are stronger acids (p. 208) than sulphuric acid, and when sulphuric acid is added to a *solution* of a nitrate or chloride it displaces hardly any of the other acids. Silica,  $\text{SiO}_2$ , the anhydride of a very weak acid, is less volatile than sulphuric acid and displaces the anhydride of the latter from sulphates when heated:



When potassium sulphate is heated with concentrated nitric acid, some potassium nitrate is formed and may be crystallised out of the solution. This is an example of *mass action* and was described by Baumé in 1773. After describing the decomposition of nitre by sulphuric acid (which he calls *vitriolic acid*) he says: 'We have just seen that vitriolic acid decomposes nitre and liberates nitric acid; but this is by the dry way. Nitric acid, in the wet way, decomposes vitriolated tartar [*i.e.*, potassium sulphate: *salt of tartar* was the old name for potassium carbonate]: this is an example of reciprocal affinity. . . . Two ounces of vitriolated tartar in powder are put into a flask and some ordinary nitric acid is poured over it. The mixture is heated until the salt dissolves, which occurs easily. The liquid is then poured into a glass capsule. It furnishes, on cooling, crystals of true nitre. The liquid is decanted and the crystals drained on porous paper, which is changed until they no longer moisten it: the nitre is then very pure and has all the properties of perfect nitre. Thus it is certain that in this operation the nitric acid has liberated the vitriolic acid and has taken to itself the alkaline base.' (Baumé, *Chymie expérimentale et raisonnée*, 1773, tome 1, p. 436.) The reaction is:

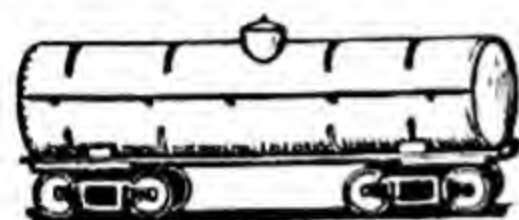


**The uses of sulphuric acid.**—Concentrated sulphuric acid, or *oil of vitriol*, is sold and transported in large glass bottles called carboys packed in iron hampers, or else in large iron tank cars or wagons. It does not attack iron when concentrated. It has

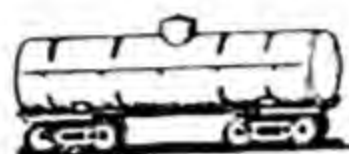


a great number of uses, which are exhibited, with an idea of the amounts of acid used in each case, by the diagrams in Fig. 243.

Sulphuric acid is used to prepare nitric and hydrochloric acids from their sodium salts, to obtain superphosphate of lime from phosphate rock for fertiliser, in the manufacture of stearin candles, in the separation of gold and silver, in cleaning ('pickling') the surface of iron sheets preparatory to coating them with tin, in making glucose from starch, in the manufacture of ether from alcohol, in making parchment paper, in



Fertiliser 44.6%



Petroleum Refining 18.3%



Chemical,  $(\text{NH}_4)_2\text{SO}_4$   
etc. 12.3%



Steel Pickling and  
Galvanising 11.7%



Metallurgical,  
Storage Batteries 8.0%



Paint, Pigments,  
Glue, etc. 2.0%



Explosives 2.0%



Textile, Finishing 1.8%

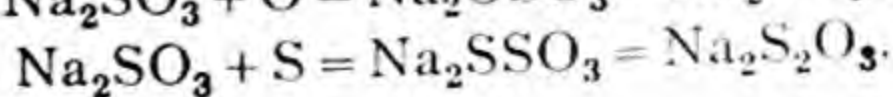
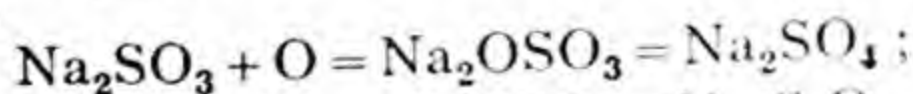


Miscellaneous 1.3%

FIG. 243.—USES OF SULPHURIC ACID.

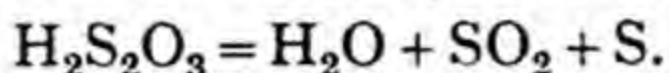
lead accumulators, in refining petroleum and other oils, in making nitroglycerin, nitrocelluloses, nitrobenzene, nitrotoluenes, picric acid and other explosives, in making phenol ('carbolic acid'), indigo, and many other organic compounds, and in the preparation of important salts such as ammonium sulphate (for fertiliser) and alum. Chemistry without sulphuric acid would hardly be recognisable, and yet we do not know who discovered this most useful substance.

**\*Sodium thiosulphate.**—Just as sodium sulphite readily takes up oxygen to form sodium sulphate, so when its solution is boiled with powdered sulphur it easily takes up sulphur to form sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$ , commonly called sodium hyposulphite or 'hypo,' the crystals of which,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , are used in photography:

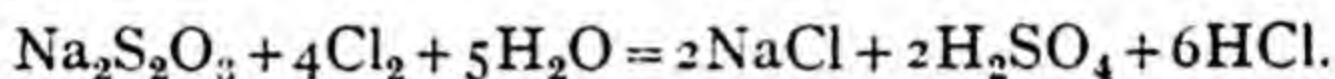


Sodium thiosulphate readily dissolves silver chloride, bromide, and iodide, forming double salts. For this reason the salt is used in photography to remove unaltered silver halides from the negatives or prints, so as to render these permanent to light ('fixing'). The double salts formed have a sweet taste.

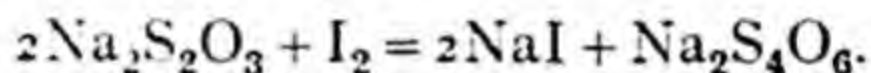
When a solution of sodium thiosulphate is acidified it rapidly deposits sulphur and smells of sulphur dioxide. If free thiosulphuric acid is formed it is rapidly decomposed :



Sodium thiosulphate in solution is readily oxidised by chlorine (hence its use as an *antichlor*, p. 326) and bromine to sulphate :



If a solution of sodium thiosulphate is added to a solution of iodine, the colour of the latter is discharged. This is used in the titration of iodine ; a little starch-paste may be added when the colour is almost discharged, and the blue colour then disappears when the last trace of iodine has reacted. The product of the reaction is not sodium sulphate, but a new salt of the formula  $\text{Na}_2\text{S}_4\text{O}_6$ , **sodium tetrathionate**, containing four atoms of sulphur ; it was discovered by Fordos and Gélis in 1843. The reaction is :





## CHAPTER XXII

### NITROGEN AND ITS COMPOUNDS

**The chemistry of nitrogen.**—Free nitrogen ( $N_2$ ) occurs in the atmosphere, of which it forms about four-fifths by volume. Traces of free nitrogen are also found in volcanic gases, and in the gases evolved from coal.

Combined nitrogen is widely distributed, and is a constituent of many important compounds. In combination with hydrogen it forms the base **ammonia**,  $NH_3$ . In combination with hydrogen and oxygen, nitrogen forms **nitrous acid**,  $HNO_2$ , and **nitric acid**,  $HNO_3$ , salts of which, the nitrates, are fairly abundant. Extensive deposits of sodium nitrate occur in Chile. Animal and vegetable organisms contain complex organic substances called **proteins**, containing an average of 16 per cent. of nitrogen. Combined nitrogen is a constituent of explosives such as gunpowder, nitroglycerine, gun-cotton, T.N.T., and picric acid; of drugs such as antipyrine, and alkaloids such as quinine and morphine; and of colouring matters such as indigo, and aniline dyes. Although free nitrogen is one of the most inert elements, its compounds exhibit a most wonderful diversity of properties, and enter readily into chemical reactions. The chemistry of nitrogen is therefore a subject of great interest and importance.

**The nitrogen cycle.**—Nitric acid is formed by electrical discharges in the atmosphere, and is washed down by rain. It is estimated that no less than 250,000 tons of nitric acid are so produced every twenty-four hours; only a small amount of this falls on fertile soil, and is utilised by plants in the form of nitrates. Leguminous plants can grow and form organic nitrogen compounds (proteins) in air and soil free from ammonia or nitrates. These plants take up atmospheric nitrogen, which is converted into organic nitrogen compounds by the agency of micro-organisms which occur in nodules called **bacteroids**, on the

roots. Certain algae, fungi, and mosses are also capable of utilising elementary nitrogen.

The nitrogen-fixing bacterium is called *Pseudomonas radicola*: there is only one general species but it has to some extent become specialised by association with particular plants. In the soil it exists as minute rods in rapid motion, but when it enters the plant by way of the root hairs, it develops into larger rods and then, when nodules are formed on the roots, these rods associate into characteristic Y-shaped organisms called *bacteroids*.

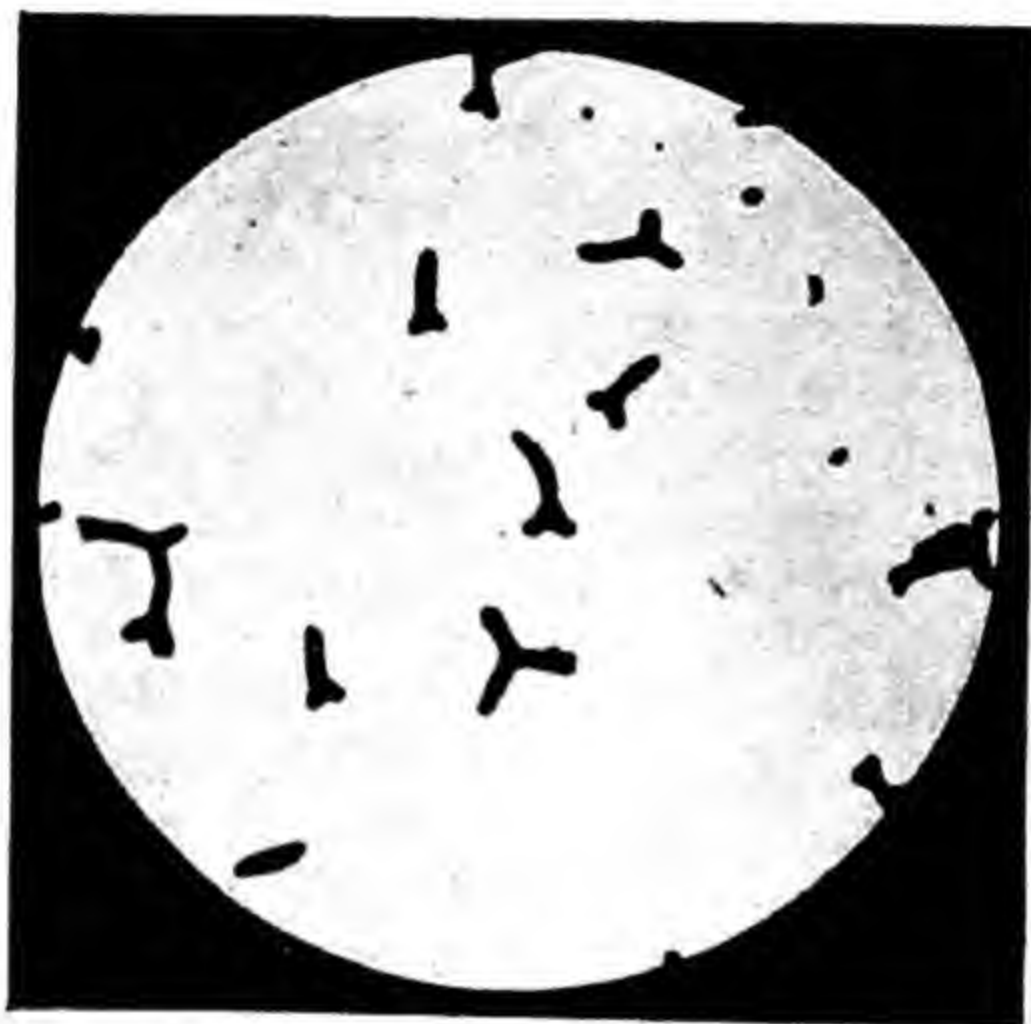


FIG. 244.—*BACILLUS RADICICOLA*.  
(Photomicrograph; Rothamsted Experimental Station.)

(Fig. 244). Other bacteria capable of fixing nitrogen are known, the most important being *Azotobacter chroococcum* (Fig. 245), which is present in soil: it is a comparatively large oval organism, which requires the presence of calcium carbonate and plays a large part in forming and maintaining the stock of combined nitrogen in the soil.

The organic nitrogen compounds elaborated by plants serve as food for herbivorous animals, and the proteins of the latter are utilised in turn by carnivora.

When the bodies of animals and plants decay, or are subjected to destructive distillation, ammonia is produced. In the soil this is oxidised by **nitrosifying bacteria** to nitrite, and by another bacterium, the **nitrifying bacterium**, the nitrite is converted into



nitrate, the latter again serving for the nourishment of plants. A portion of the fixed nitrogen is again set free by the action of **denitrifying bacteria** in the soil. Both nitrosifying bacteria and the nitrifying bacterium derive their carbon from carbon dioxide.

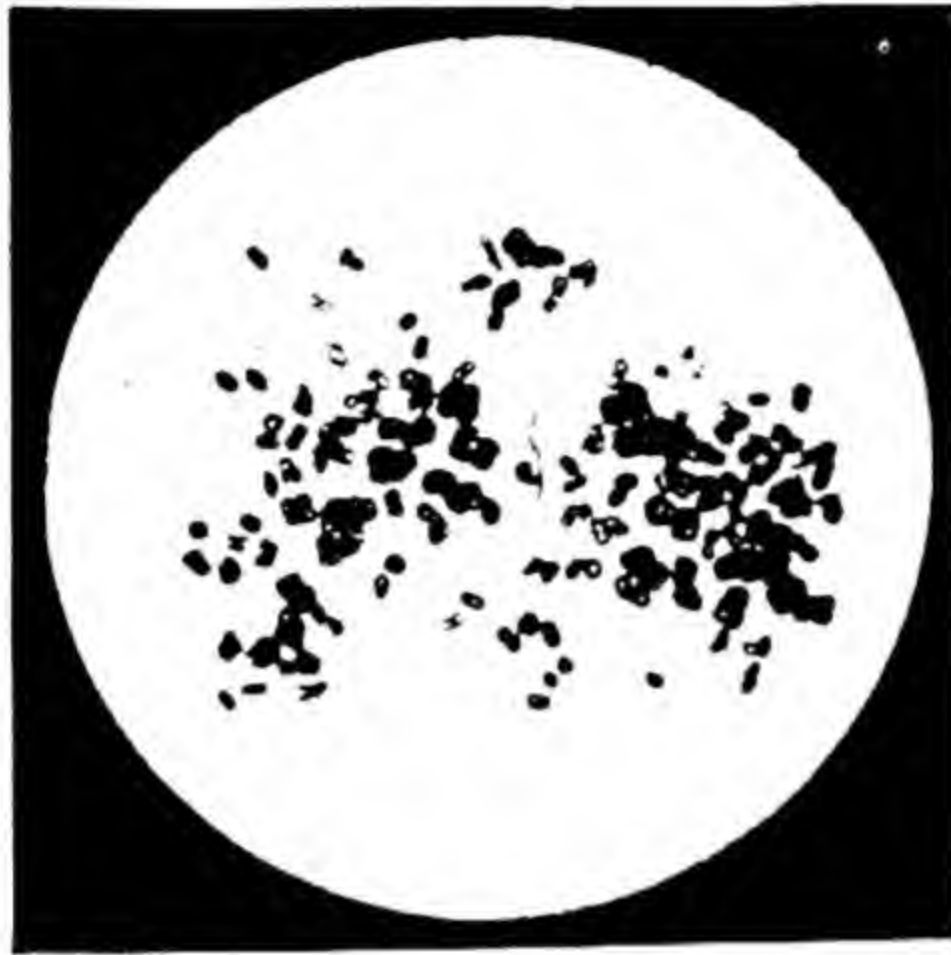
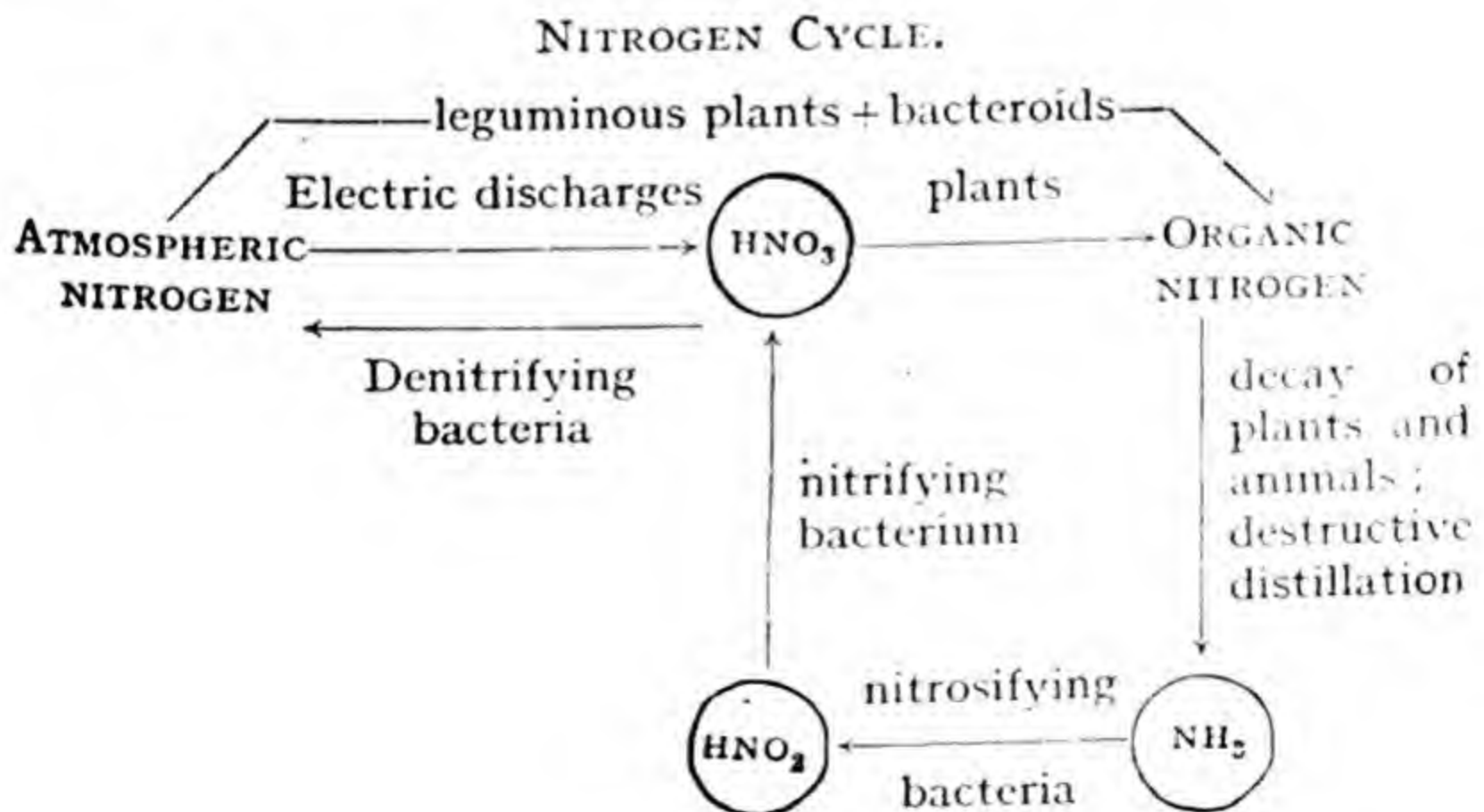


FIG. 245.—AZOTOBACTER.  
(Photomicrograph ; Rothamsted Experimental Station)

The nitrogen cycle in Nature may be represented diagrammatically as shown below.



The bacterium which produces nitrites is *B. nitrosomonas* and there appear to be several varieties of it ; that which converts nitrites into nitrates is *B. nitrobacter*, and only one variety is known.

### THE ATMOSPHERE.

**The atmosphere.**—The early experiments on the composition of the atmosphere, described in Chapter V, showed that the principal constituents are two gases, oxygen, which was described in Chapter XVI, and nitrogen, the chemistry of which will be described in the present chapter.

In 1772, Daniel Rutherford allowed mice to breathe in air under a bell-jar, and removed the fixed air (carbon dioxide) by washing the residual gas with potash. A gas remained, which he called *mephitic air*, since it did not support combustion or respiration ; unlike fixed air, it was not absorbed by alkali or lime-water. Priestley (1772) burnt charcoal in a confined volume of air, and absorbed the fixed air with alkali, also obtaining mephitic air, which he called *phlogisticated air*.

Scheele (1772) first clearly recognised that air is a mixture of two gases, one of which (*fire air*) supports combustion and respiration, while the other (*foul air*) does not. Lavoisier's experiment (1775-6) (p. 101) furnished a decisive proof of this result, although both gases had been separately prepared by Scheele, who also showed that, when they were mixed in proper proportions, common air was formed. Lavoisier gave to Scheele's foul air the name azote (Greek  $\alpha$ , no ;  $zoe$ , life), which is still used in France ; the German name *Stickstoff* is based on the same property. The English name nitrogen (Greek *nitron*, nitre) was suggested by Chaptal in 1790.

Atmospheric nitrogen was considered to be a pure substance until 1894, when Rayleigh and Ramsay found that it contained about 1 per cent. of an inert gas which they called **argon**. Argon occurs in air mixed with nitrogen and oxygen and some other inert gases in small amounts.

The composition of air, freed from moisture and carbon dioxide, is roughly 4 volumes of nitrogen to 1 volume of oxygen ; the exact figures (Leduc, 1896) are :

	By weight.	By volume.
Nitrogen - -	75.5	78.06
Oxygen - -	23.2	21.00
Argon, etc. - -	1.3	0.94



Although the composition of air *freed from moisture and carbon dioxide* is surprisingly constant, it is in reality *slightly* variable according to locality and at different times in the same place. If we consider air which contains the variable amount of water vapour always present in it, the percentage of oxygen will vary quite appreciably according to the humidity or moistness of the air.

**The composition of air by volume.**—In determining the volumetric composition of air, the oxygen is extracted by exposing a measured volume of air to burning phosphorus, phosphorus in the cold, moist iron filings, potassium sulphide, or an alkaline solution of pyrogallol. The first and last remove oxygen rapidly; the others slowly. The contraction gives the oxygen and the residual gas is the nitrogen. The pressure and temperature must remain the same during the experiment, or a correction applied, in accurate work.

When burning phosphorus is used, a porcelain capsule containing a small piece of phosphorus is floated on water in a glass trough, and covered with a stoppered bell-jar divided into five parts (Fig. 246), the water in the trough being adjusted to the lowest mark. The phosphorus is then ignited by a piece of wire heated at one end, and the stopper at once inserted. The phosphorus burns, with the production of white fumes of phosphorus pentoxide, until the oxygen is removed from the air. The apparatus is allowed to stand until it is cold and the fumes have dissolved in the water, forming phosphoric acid. The water levels are again adjusted, when it will be found that the residual gas occupies four volumes. A lighted taper inserted into this gas is extinguished. This experiment shows that air contains approximately one volume of oxygen associated with four volumes of nitrogen. The experiments with phosphorus in the cold, moist iron filings, and potassium sulphide have been described on p. 96.

The experiment with alkaline pyrogallol is carried out as follows. A long glass tube closed at one end and fitted with a rubber stopper at the other, is taken, and a solution of

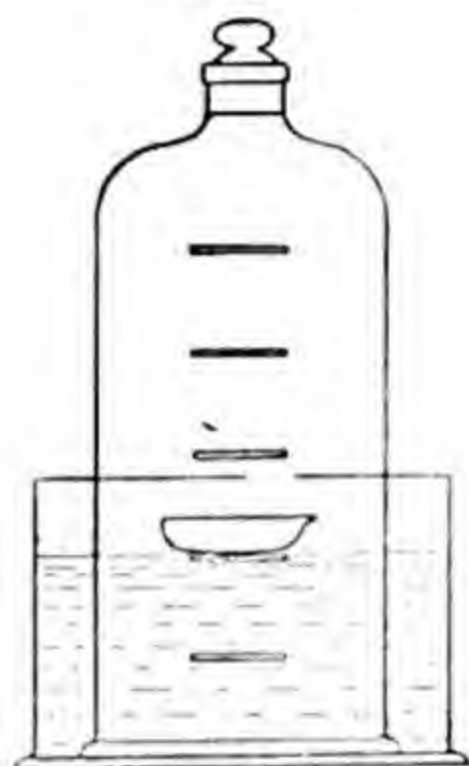
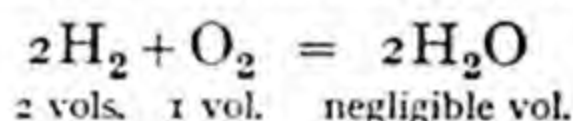


FIG. 246.—APPARATUS FOR BURNING PHOSPHORUS IN A CONFINED VOLUME OF AIR.

pyrogallol poured in so as to fill one sixth of the tube, the latter being previously divided into six parts by rubber bands. A *small* piece of solid caustic soda is slid into the upper part by means of crucible tongs, taking care that it does not fall into the liquid. The stopper is inserted and the tube shaken. The liquid becomes black owing to absorption of oxygen. The tube is opened under water : one of the remaining five divisions fills with water, and four-fifths of the original volume of air remains as nitrogen.

The most *accurate method* of finding the percentage by volume of oxygen in air is to explode a measured volume of air in a eudiometer over mercury with excess of hydrogen. The hydrogen unites with the oxygen to form water, which condenses to a liquid of negligible volume, hence the volume of oxygen is found by taking *one third* of the measured contraction :



Since the residual gas is measured moist, the initial mixture of hydrogen and air should also be saturated with water vapour by passing a few drops of water into the eudiometer graduated in millimetres before measuring the gases.

The following readings were taken in an experiment by Bunsen :

Vol. of air	(at S.T.P.)	428.9 mm.
Vol. of air + H <sub>2</sub>	„	749.8 mm.
Vol. after explosion	„	480.1 mm.

$$\therefore \text{vol. of oxygen} = (749.8 - 480.1)/3 = 89.9 \text{ mm. ;}$$

$$\therefore \text{vol. of nitrogen} = 428.9 - 89.9 = 339.0 \text{ mm. ;}$$

$$\therefore \text{vol. of oxygen in 100 vols. air} = \frac{100}{428.9} \times 89.9 = 20.9 ;$$

$$\therefore \text{vol. of nitrogen in 100 vols. air} = 100 - 20.9 = 79.1 ;$$

$\therefore$  air contains 20.9 per cent. of oxygen and 79.1 per cent. of nitrogen (and argon) by volume.

**The gravimetric composition of air.**—The determination of the composition of air *by weight* is carried out by the method of Dumas and Boussingault (1841). A long tube of hard glass is packed with bright copper turnings and fitted with a stopcock at each end. It is exhausted, weighed, and connected at one end with a large weighed vacuum globe, closed by a stopcock, and at the other with a bulb of potash solution and two U-tubes,



one containing solid caustic potash and the other (next to the tube containing the copper) calcium chloride, which remove carbon dioxide and moisture from the air (Fig. 247).

The tube containing the copper is heated to bright redness in a furnace. The stopcocks are then slightly opened and air allowed to pass *slowly* over the heated copper, the oxygen being absorbed to form copper oxide and the nitrogen passing on into the globe. When the globe is full of nitrogen the stopcocks are closed and the apparatus allowed to cool. The globe is weighed and the weight of the nitrogen it contains is found. The tube containing the copper and copper oxide is now weighed. The

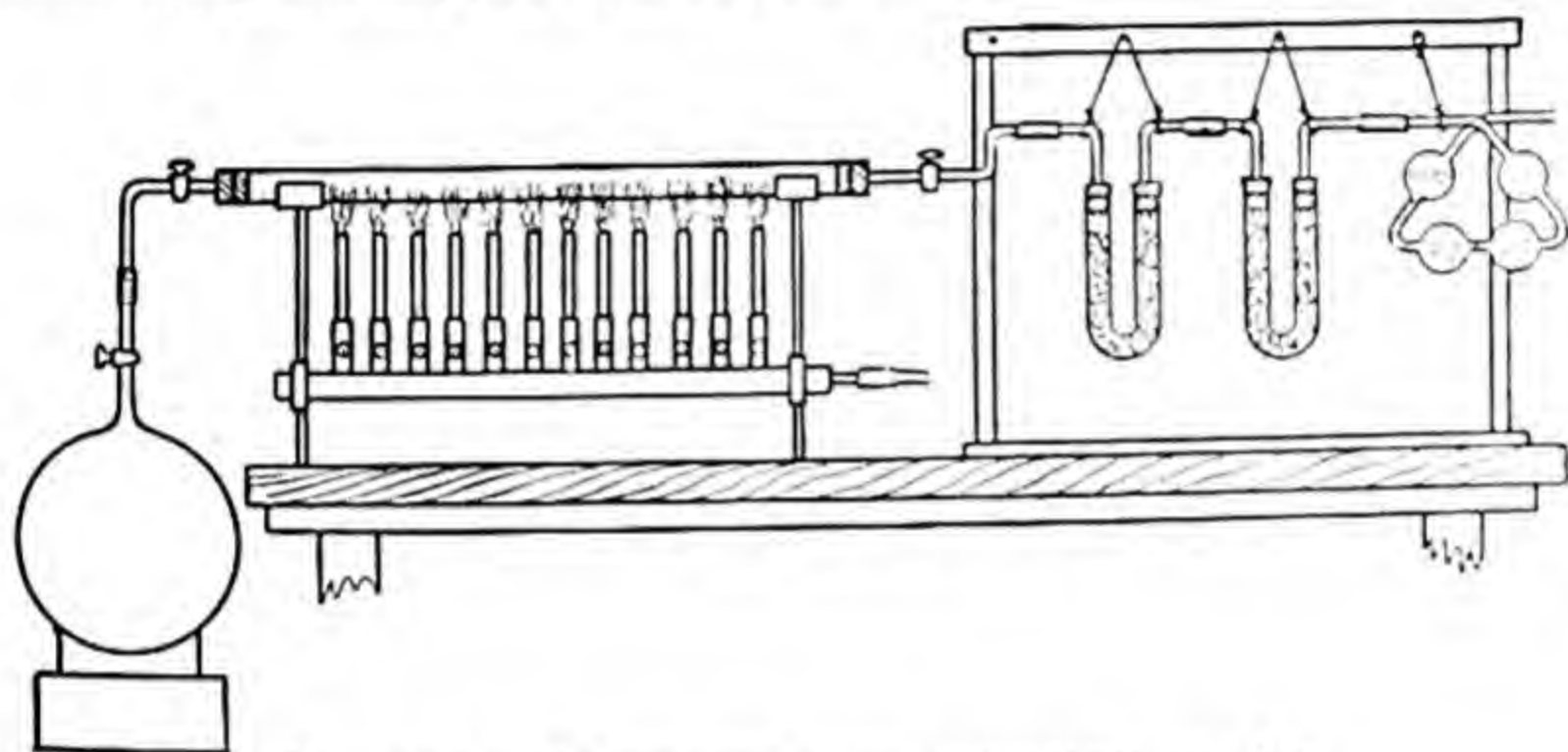


FIG. 247.—GRAVIMETRIC COMPOSITION OF AIR.  
DUMAS AND BOUSSINGAULT'S APPARATUS (MODIFIED).

*nitrogen in this tube* is now removed by a pump and the *vacuous* tube again weighed in order to find the weight of this nitrogen to be added to that in the globe. The increase in weight of the *vacuous* tube gives the weight of oxygen. The nitrogen as weighed contains the argon and other inert gases. These can be determined by repeatedly passing the nitrogen over red-hot magnesium, when only the inert gases remain, the nitrogen forming magnesium nitride.

**Air is a mixture, not a chemical compound.**—That air is a mixture (really a solution, see p. 55) and not a compound of oxygen and nitrogen follows from the facts given below :

(i) Although the composition (when freed from water and carbon dioxide) is *nearly* constant, it is not quite so, whereas every compound has a definite composition.

(ii) The constituents of air may be partially separated by

diffusion through a porous pipeclay tube into a vacuum (*atmolysis*), when the nitrogen diffuses more rapidly than the oxygen (see Graham's law, p. 162).

(iii) The constituents of air may be separated by the fractional distillation of liquid air (p. 276).

(iv) When air is shaken with water, the dissolved part is richer in oxygen than the undissolved part (p. 34).

(v) When oxygen and nitrogen are mixed together there is no evolution or absorption of heat and the properties of the mixture are intermediate between those of the constituents.

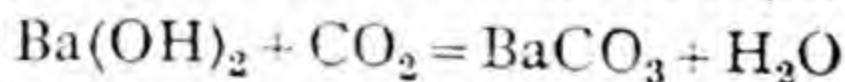
(vi) If air were a compound,  $N_4O$ , its vapour density would be  $\frac{1}{2}(4 \times 14 + 16) = 36$ , whereas it is actually 14.4, which corresponds with the mixture  $4N_2 + O_2$ .

**Variable constituents of air.**—Besides oxygen, nitrogen and inert gases, air always contains a nearly constant amount of carbon dioxide (about 3 volumes in 10,000 of *dry* air), and varying amounts of water vapour. It may also contain very small amounts of ammonia, nitric acid and nitrates, ozone, and sometimes other substances (hydrogen, hydrocarbons) in minute amounts.

The following table gives the average percentage composition of *dry* air by volume. The estimated total weight of the atmosphere is about  $51 \times 10^{17}$  kgm.

Nitrogen	-	78.03	Neon	-	-	0.0015
Oxygen	-	20.99	Helium	-	-	0.0005
Argon	-	0.9323	Krypton	-	-	0.0001
Carbon dioxide	0.03		Xenon	-	-	0.000009

**Estimation of moisture and carbon dioxide in air.**—The moisture and carbon dioxide in air may be estimated by aspirating a known volume of air first through weighed calcium chloride tubes to absorb moisture, and then through weighed tubes of solid caustic potash to absorb carbon dioxide. Generally the amount of moisture is found by physical methods (*hygrometry*), and that of carbon dioxide by shaking a known volume of the air with standard baryta solution, and titrating the residual baryta with oxalic acid (*Pettenkofer's method*):

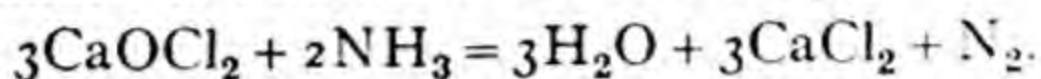




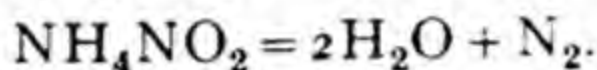
## NITROGEN.

**Preparation.**—Nitrogen may be prepared from air by removing the oxygen by burning phosphorus or by red hot copper. This atmospheric nitrogen is not quite pure, since it contains rather more than 1 per cent. by volume of inert gases (argon, etc.). These do not usually interfere with the use of the nitrogen, but pure nitrogen must be prepared by chemical methods, from compounds of nitrogen.

Nitrogen may be prepared by adding a paste of bleaching powder to ammonia in a flask and warming :

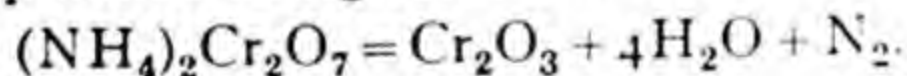


The most convenient method for the preparation of nitrogen in the laboratory is by gently heating a solution of ammonium nitrite :



Instead of ammonium nitrite, a solution of sodium nitrite and ammonium sulphate or chloride is generally used. These salts produce, by double decomposition, ammonium nitrite and sodium sulphate or chloride, and the former then decomposes as explained.

Ammonium dichromate (red crystals) decomposes violently on heating, nitrogen, water, and a voluminous green residue of chromium sesquioxide being formed :

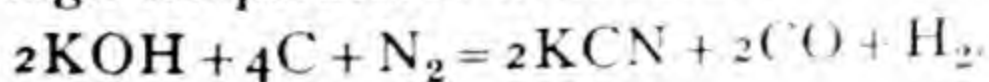


Nitrogen may be collected over water, since it is only slightly soluble. It can be dried by calcium chloride or sulphuric acid.

Nitrogen is prepared technically from air either by passing over heated copper or (more usually) by the fractional distillation of liquid air (p. 276).

**Properties of nitrogen.**—Nitrogen is a colourless, odourless, tasteless gas ; it does not support combustion, or respiration, although it is not poisonous ; it does not turn lime water milky. It is sparingly soluble in water, and has no action on litmus. Nitrogen can be liquefied by strong cooling and pressure, but with greater difficulty than oxygen.

Nitrogen is an inert element, but it combines directly with oxygen, hydrogen, boron, calcium, and magnesium. Compounds of elements with nitrogen are called nitrides, e.g.,  $\text{Ca}_3\text{N}_2$ ,  $\text{Mg}_3\text{N}_2$ ,  $\text{BN}$ . In presence of alkalis, or baryta, it also combines at high temperatures with carbon to form cyanides :



Oxygen or hydrogen combines with nitrogen on sparking; the metallic nitrides are formed by passing nitrogen over the element heated to redness. By the action of water they give ammonia:

$$\text{Ca}_3\text{N}_2 + 6\text{H}_2\text{O} = 2\text{NH}_3 + 3\text{Ca}(\text{OH})_2.$$

### AMMONIA.

The most important compound of nitrogen and hydrogen is **ammonia**,  $\text{NH}_3$ , traces of which occur in the atmosphere: bottles containing hydrochloric acid slowly become coated with ammonium chloride. **Ammonium chloride**,  $\text{NH}_4\text{Cl}$ , and **sulphate**,  $(\text{NH}_4)_2\text{SO}_4$ , occur in volcanic districts. Small quantities of ammonium salts occur in plants and animals (e.g., in blood and in urine), in rock salt, in the soil, and in natural waters (as nitrite and nitrate).

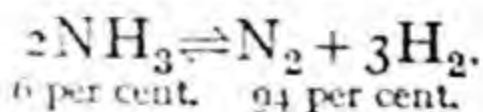
Ammonia is produced when organic matter containing nitrogen is strongly heated ('destructive distillation'): hair, bones, feathers, glue, coal, horn, etc., all give off ammonia in this way, hence it was formerly called *spirit of hartshorn*.

Ammonium chloride was apparently first obtained in Egypt from the soot produced by burning dry camels' dung, used as a fuel. It received the name *sal ammoniac*. It was also obtained from the volcanoes of Central Asia.

Gaseous ammonia was first obtained by Priestley in 1774, and collected over mercury; he called it *alkaline air*, and found that when electric sparks were passed through it twice the volume of a combustible gas was formed. This was confirmed by Berthollet:



**Synthetic ammonia.**—Ammonia is formed *from its elements* when these are sparked together:  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ . This appears to have been discovered by Regnault (1840). The reaction is reversible, and a state of equilibrium is set up in which 6 per cent. of  $\text{NH}_3$  exists with 94 per cent. of the uncombined gases. If the mixture  $\text{N}_2 + 3\text{H}_2$ , and pure ammonia, respectively, are exposed to prolonged sparking, contraction ensues in the first case and expansion in the second, until the volumes and compositions are the same:



The direct combination of nitrogen and hydrogen is utilised in the **Haber process** (1905) for the production of ammonia.

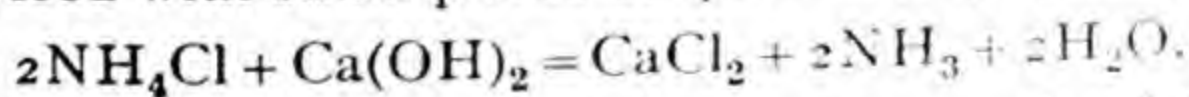


Since a diminution of volume occurs in the reaction:  $N_2 + 3H_2 = 2NH_3$ , the amount of ammonia formed in equilibrium will increase with the pressure (see p. 229). Since heat is evolved in the reaction, the amount of ammonia in the equilibrium state will diminish with rise of temperature.

The process is now the main source of ammonia. It is carried out by circulating a mixture of very pure hydrogen and nitrogen in the correct proportions, under high pressure (200 atm.) over a heated *catalyst* consisting of iron with some other material (called a *promoter*), such as molybdenum, or potassium and aluminium oxides. The ammonia formed is removed by liquefaction or by solution in water, and the residual gas, dried if necessary, is again circulated over the catalyst (Fig. 248). In the **Claude process** higher pressures (up to 1000 atm.) are used.

Very large quantities of synthetic ammonia are now made, especially in Germany. There is also a large works at Billingham, in England, belonging to Imperial Chemical Industries Ltd., and synthetic ammonia works are either in operation or under construction in most countries in the world.

**Laboratory preparation.**—Ammonia gas is prepared by heating the concentrated solution in a flask, or by heating a mixture of ammonium chloride with dry slaked lime in a flask, the mixture being covered with small pieces of quicklime (Fig. 249):



The gas is dried by passing through a tower of quicklime and collected by upward displacement, since it is much lighter than air. (Ammonia gas cannot be dried by calcium chloride or sulphuric acid, both of which absorb it.)

Ammonia is also formed by the reduction of oxygen

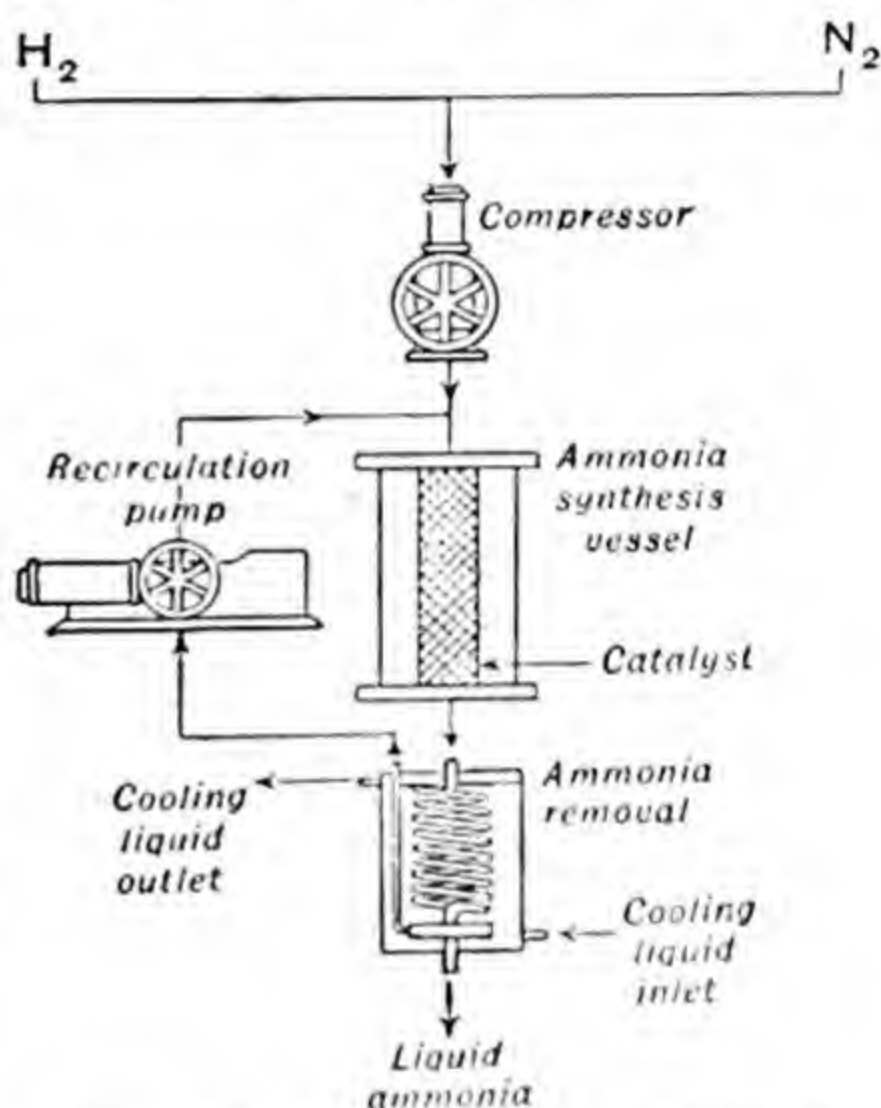
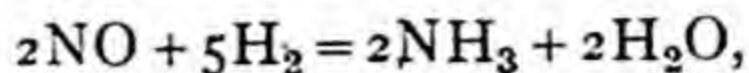
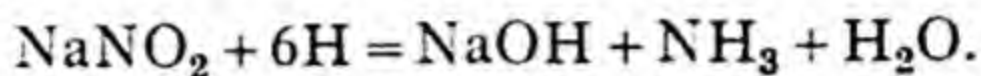


FIG. 248.—SYNTHETIC AMMONIA APPARATUS (DIAGRAMMATIC).

compounds of nitrogen, *e.g.*, by passing a mixture of nitric oxide and hydrogen over heated spongy platinum, when a vigorous reaction occurs :



or by heating zinc with a solution of a nitrate or nitrite and caustic soda :



Ammonia is recovered technically from the ammoniacal liquor of gas-works or coke-ovens (p. 444). This is distilled,

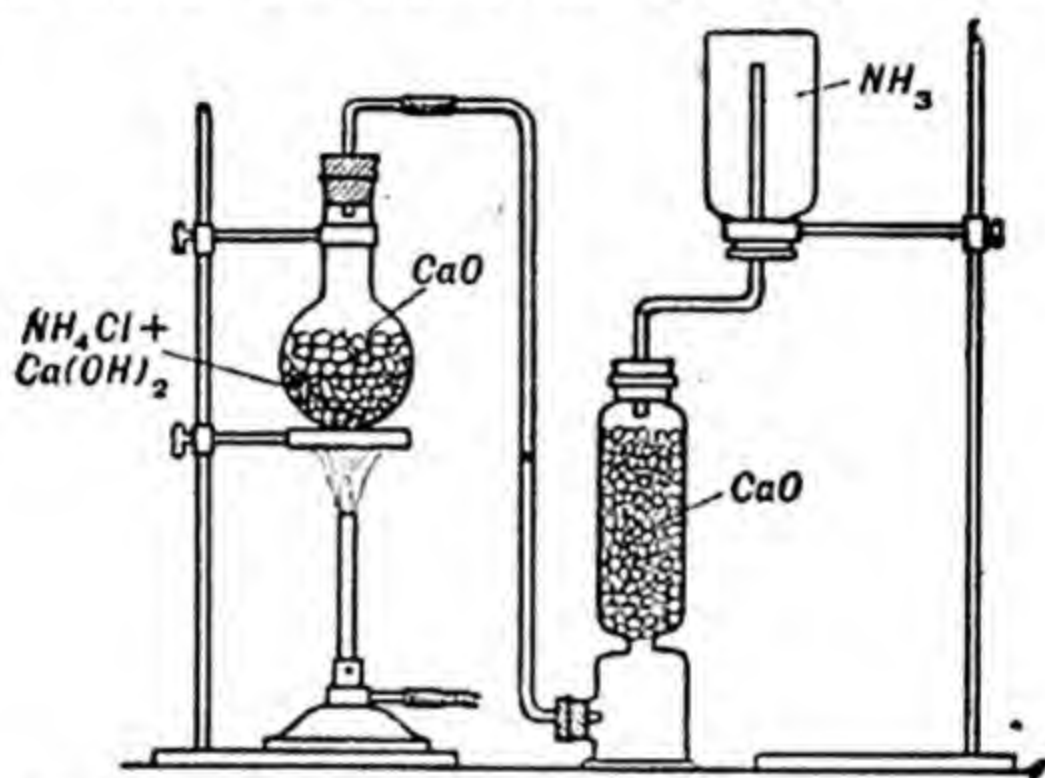
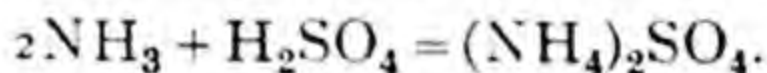


FIG. 249.—LABORATORY PREPARATION OF AMMONIA GAS.

after the addition of milk of lime, and the ammonia condensed in sulphuric acid to form ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , used as a fertiliser :

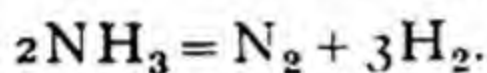


The source of this ammonia is the small quantity of combined nitrogen (about 1 per cent.) in bituminous coal.

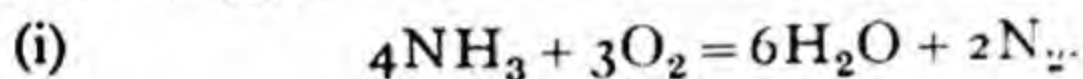
**Properties of ammonia.**—Ammonia is a colourless gas with a characteristic pungent odour, and lighter than air. It is easily liquefied by cold or pressure to a colourless liquid, *anhydrous ammonia*, which is manufactured for use in refrigerating machinery and is sold in large steel cylinders. The gas is very soluble in water, forming an alkaline solution containing ammonium hydroxide  $\text{NH}_4\text{OH}$ . The solubility may be shown by the 'fountain experiment' (p. 320), using water containing red litmus, which turns blue. A nearly saturated solution of ammonia has a specific gravity of 0.880 : it smells very strongly of ammonia. Heat is given out when the gas passes into



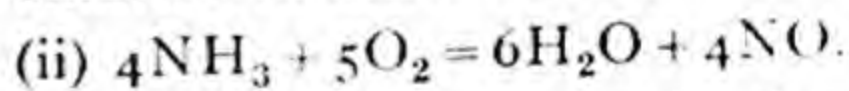
solution, and if the ammonia is removed by forcing a stream of air through the concentrated solution there is a considerable fall in temperature, so that a flask in which the experiment is performed may be frozen to a block of wood if a little water is interposed between them. Ammonia is not combustible in air, neither does it support combustion. The flame of a taper brought into a jar of ammonia, before it is extinguished, is surrounded by a large greenish-yellow flame, produced by the combustion of the hydrogen set free from the ammonia by heat:



If a current of ammonia gas is passed through a tube surrounded by a wider tube through which oxygen is passing, the ammonia burns readily in the oxygen with a large yellowish-green flame (Fig. 250). A mixture of ammonia gas and oxygen explodes when kindled by a taper:



In presence of heated platinum as a catalyst, a mixture of ammonia with air or oxygen is oxidised to nitric oxide;



These two modes of oxidation may be illustrated by the following experiment.

A mixture of oxygen and ammonia is produced when oxygen is bubbled through concentrated ammonia heated in a flask. If a heated platinum spiral is hung in the neck of the flask (Fig. 251), the mixture of ammonia and oxygen ignites with a feeble explosion, combustion occurring according to

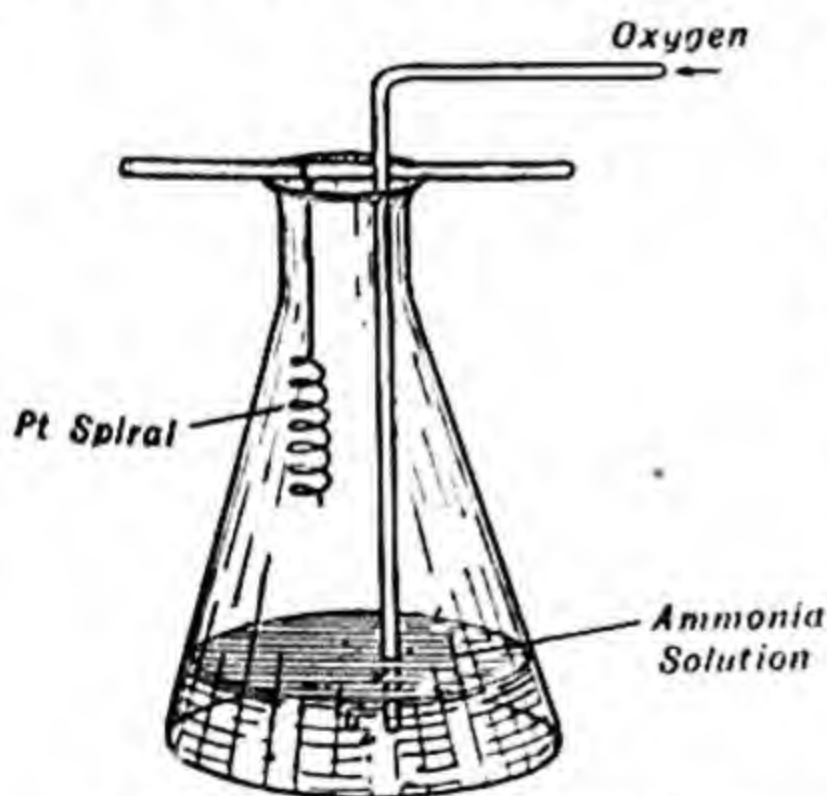


FIG. 251.—THE CATALYTIC OXIDATION OF AMMONIA.

reaction (i). The glowing wire then begins to oxidise the ammonia according to reaction (ii), red gaseous higher oxides

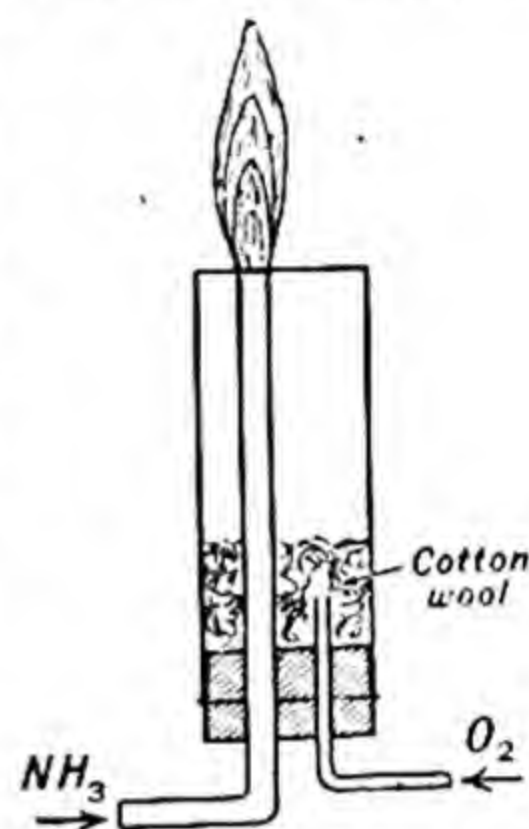
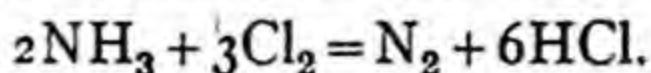


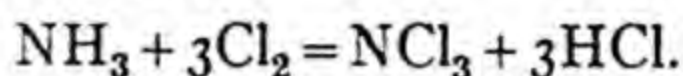
FIG. 250.—AMMONIA BURNING IN OXYGEN.

of nitrogen and white fumes of ammonium nitrate being formed. This period is succeeded by another explosion, and so on.

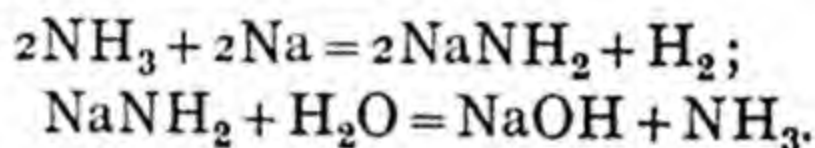
Chlorine decomposes ammonia with liberation of nitrogen :



With *excess of chlorine* a violently explosive oily liquid, **nitrogen trichloride**,  $\text{NCl}_3$ , is formed :



Concentrated ammonia solution reacts with iodine to give a black, explosive powder called **nitrogen iodide**,  $\text{NI}_3 \cdot \text{NH}_3$ . When ammonia gas is passed over heated sodium, hydrogen is evolved and sodamide,  $\text{NaNH}_2$ , is formed. Water decomposes sodamide with the formation of ammonia :



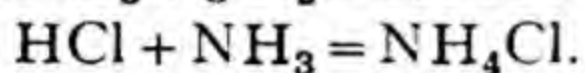
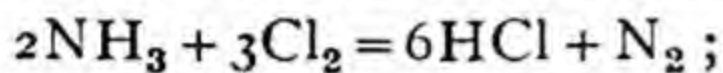
**Tests for ammonia.**—The gas is detected by its smell, by turning red litmus paper blue, and by producing white fumes of ammonium chloride with hydrochloric acid. In solution, free ammonia in excess produces a deep blue colour with copper salts, and traces of both free ammonia or ammonium salts produce a brown coloration or precipitate with *Nessler's reagent*, a solution of potassium mercuri-iodide containing excess of caustic potash.

**The composition of ammonia.**—The composition of ammonia may be found in several ways. In one method a measured volume of ammonia gas is decomposed into nitrogen and hydrogen by *prolonged* sparking in a eudiometer (see p. 378). In an experiment 20 c.c. of ammonia gas on sparking expanded (almost) to 40 c.c. (a little ammonia remains undecomposed). Oxygen was added in excess, and on passing a spark the hydrogen and oxygen combined to form water :  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$  (liquid) and there was a contraction of 45 c.c. ;  $\therefore$  vol. of hydrogen  $= \frac{2}{3} \times 45 = 30$  c.c. ;  $\therefore$  vol. of nitrogen  $= 40 - 30 = 10$  c.c. Hence 2 vols. of ammonia gas give 1 vol. of nitrogen and 3 vols. of hydrogen, and so, by Avogadro's hypothesis, 1 molecule (2 atoms) of nitrogen and 3 molecules (6 atoms) of hydrogen give 2 molecules of ammonia, or 1 molecule of ammonia contains 1 atom of nitrogen and 3 atoms of hydrogen, and the formula is  $\text{NH}_3$ . This can be *confirmed* by the density, which shows that the molecular weight is 17.

A convenient method of demonstrating the composition of



ammonia is **Hofmann's method**. A long glass tube closed at one end and provided with a wide stopcock (Fig. 252) is divided below the stopcock into three equal volumes by rubber bands and is filled with chlorine. The tube above the stopcock is one-third filled with concentrated ammonia solution, which is added drop by drop to the chlorine. Each drop reacts with a yellowish-green flame, and the formation of white clouds of ammonium chloride

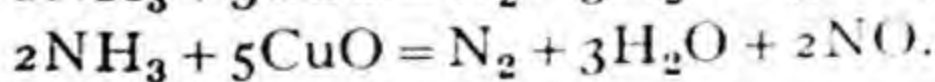
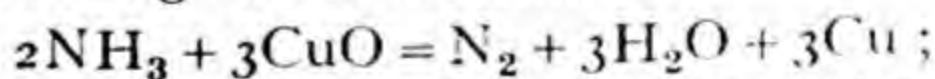


The fumes are washed down by shaking, and dilute sulphuric acid is then added to fix the excess of ammonia.

The tube is cooled by immersing in a large cylinder of water, and the upper part above the tap is fitted with a cork and siphon tube dipping into previously boiled water, as shown, the whole being filled with water. On opening the tap, water enters the tube, and the residual nitrogen occupies 1 volume.

The 3 vols. of chlorine have combined with 3 vols. of hydrogen from the ammonia to form HCl, therefore 1 vol. of nitrogen is combined in ammonia with 3 vols. of hydrogen. Since nitrogen and hydrogen both have molecules containing two atoms, the ammonia molecule contains nitrogen and hydrogen atoms in the ratio 1 to 3, and the density shows that molecular weight is 17 ; hence the formula is  $\text{NH}_3$ .

When dry ammonia gas is passed over red-hot copper oxide, the latter is reduced and the ammonia undergoes oxidation. Both nitrogen and nitric oxide are produced, together with water vapour, according to the reactions :



If, however, the copper oxide is followed by a long layer of metallic copper heated to *bright redness*, the nitric oxide is decomposed and nitrogen passes on

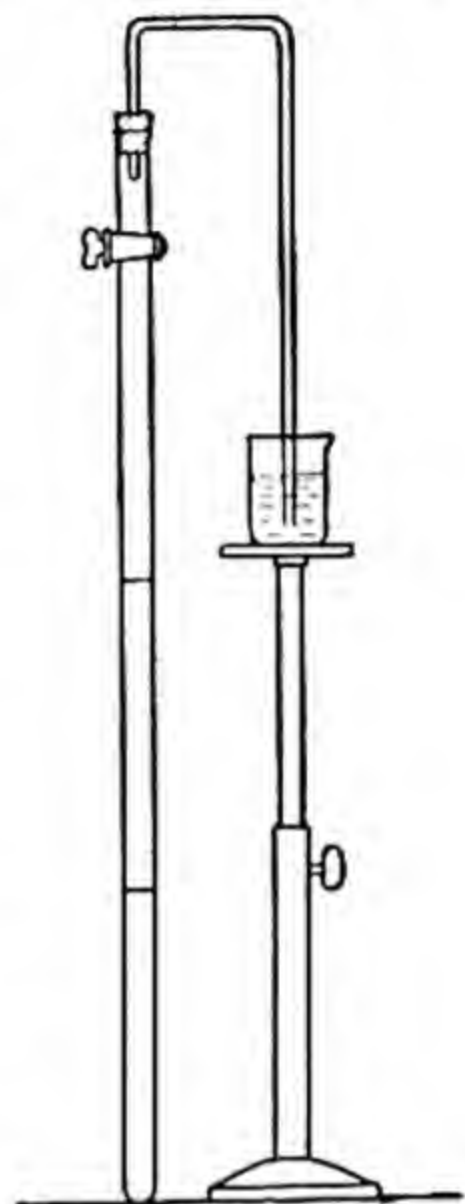
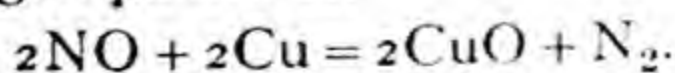


FIG. 252. — VOLUMETRIC COMPOSITION OF AMMONIA.

The water vapour may be absorbed in weighed calcium chloride tubes and the nitrogen collected in a weighed exhausted globe, and the method may then be used to find the composition of ammonia by weight.

**Oxides and oxyacids of nitrogen.**—Oxygen and nitrogen combine in five proportions to give five oxides of nitrogen, two of which are anhydrides of nitrous acid and nitric acid, respectively :

Nitrous oxide,  $N_2O$ ,

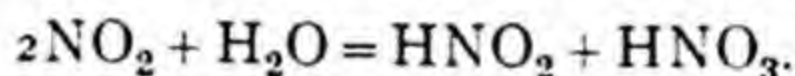
Nitric oxide,  $NO$ ,

Nitrogen trioxide,  $N_2O_3$ , the anhydride of nitrous acid,  $HNO_2$ ,

Nitrogen dioxide,  $NO_2$  or  $N_2O_4$ ,

Nitrogen pentoxide,  $N_2O_5$ , the anhydride of nitric acid,  $HNO_3$ .

Nitrogen dioxide gives both nitrous and nitric acids with water :



Nitric oxide is formed by passing sparks through air (Fig. 253) : it combines with the excess of oxygen to form nitrogen dioxide, and when the gas is shaken with litmus solution the dioxide dissolves forming nitrous and nitric acids, which turn the litmus red.

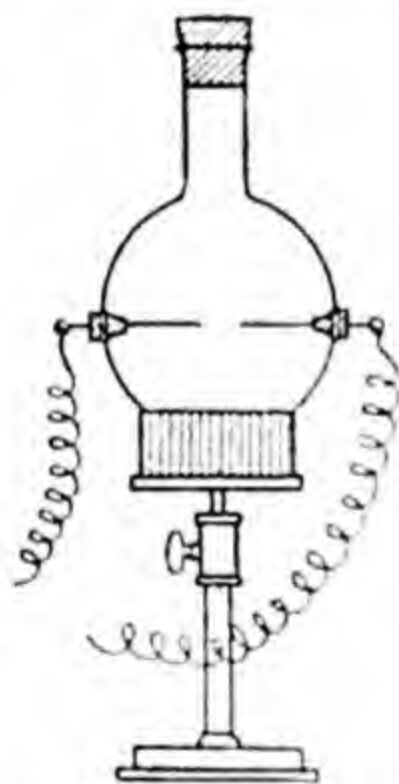


FIG. 253.—THE FORMATION OF OXIDES OF NITROGEN BY PASSING ELECTRIC SPARKS THROUGH DRY AIR.

**The fixation of nitrogen by the arc process.**—Although nitrogen is not a combustible gas in the ordinary sense—if it were there would be no atmosphere—yet it may be caused to burn with a true flame. The combustion of nitrogen, so far from giving out heat and so being capable of maintaining itself when once started, is attended by a very considerable absorption of heat : it is an **endothermic reaction**, which occurs when energy is supplied. If the two electrodes of a twelve-inch spark coil are fully separated,

the spark is blue, jagged and very noisy, and ozone is produced in the air around it. If the electrodes are brought near together, the character of the discharge alters : it becomes greenish-yellow in colour, and quiet. The result is a true flame, the atmospheric nitrogen and oxygen combining in it to form nitric oxide,  $NO$ .



The process has been used on an immense scale in Norway, where electrical energy is obtained from water-power coming from melting snow—'white coal'—to obtain nitric acid from atmospheric nitrogen, the 'fixation of nitrogen.' The electric flame is spread out by a powerful magnet into an apparent disc (really an optical illusion caused by the rapid spring of the arch-shaped filament of the arc discharge from one side to the other), burning inside a box of refractory material through which air is passed. About one per cent. of the nitrogen is converted into nitric oxide. The very hot gas is passed through coolers, including boiler tubes, then the cool gas goes through a

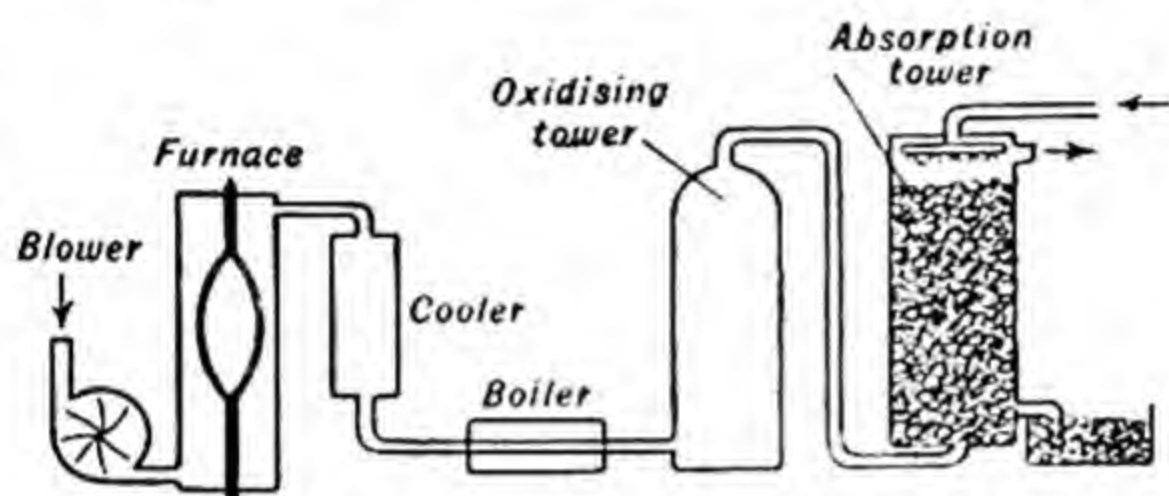
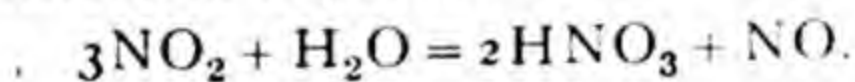


FIG. 254.—DIAGRAM OF THE ARC PROCESS FOR PRODUCING NITRIC ACID FROM THE ATMOSPHERE.

large empty tower to allow the NO to oxidise to  $\text{NO}_2$ , which takes place rather slowly, and this is absorbed in large granite towers packed with stone, down which water is trickling (Fig. 254). Nitric acid is produced :

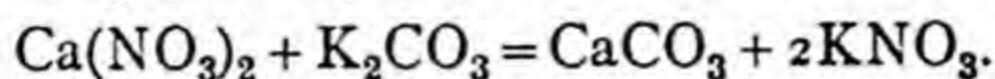


The NO is re-oxidised to  $\text{NO}_2$  by the excess of air until nearly all the oxides of nitrogen are absorbed as nitric acid, which may be neutralised with limestone to form calcium nitrate ('Norge saltpetre'). The weak nitrous gases from the last absorption tower pass through a tower for treatment with sodium carbonate solution, when a mixture of sodium nitrate and nitrite is formed.

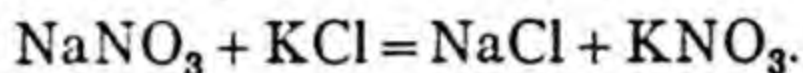
**Nitre or saltpetre.**—If soil containing decomposing nitrogenous organic matter is mixed with lime or calcium carbonate, such as old mortar, calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , is produced. This arises from the oxidation of the organic matter, in the presence of feeble alkalies, by micro-organisms (p. 369).

This calcium nitrate can be extracted by water and decomposed by wood-ashes (potassium carbonate), when calcium

carbonate is precipitated and the filtrate yields crystals of potassium nitrate,  $\text{KNO}_3$ , on evaporation :



This salt, known as nitre, or saltpetre, is still made in this way in India, but it is usually manufactured from sodium nitrate (Chile saltpetre) and potassium chloride, as explained on p. 41 :



Potassium nitrate is chiefly used in making gunpowder (*q.v.*), also in pickling meat and hams, to which it imparts a red colour. Fused potassium nitrate is a powerful *oxidising agent*: sulphur and carbon burn on its surface brilliantly (p. 90).

Sodium nitrate,  $\text{NaNO}_3$ , is found in an impure form, called *caliche*, in great beds in the rainless districts of Chile. When purified it is called *Chile saltpetre*, or *Chile nitre*, and used as a fertiliser and for the manufacture of nitric acid.

**Nitric acid.**—This acid, called *aqua fortis*, was known to the alchemists and appears to have been discovered about

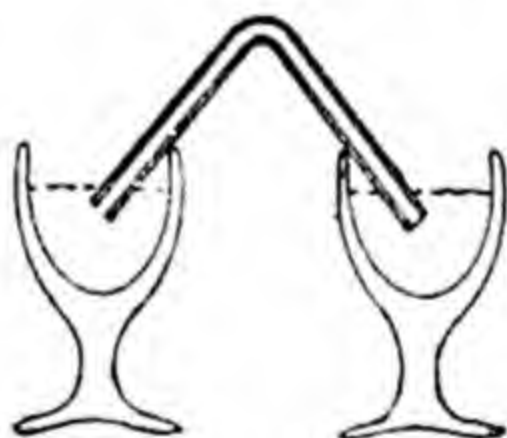


FIG. 255.—CAVENDISH'S APPARATUS FOR SPARKING AIR AND OXYGEN OVER POTASH SOLUTION.

1100, although the present method of preparation is first described by Glauber. Lavoisier in 1776 showed that nitric acid gave nitric oxide and oxygen on decomposition, but he did not know that nitric oxide is a compound of nitrogen and oxygen. This was proved by Cavendish in 1785. Cavendish passed electric sparks for a long time through a mixture of air and oxygen confined over mercury in a tube containing some potash solution. The tube connected two cups containing mercury, into which the wires from an electrical machine dipped (Fig. 255). The gas contracted and a solution of nitre was formed. When the excess of oxygen



was absorbed by potassium sulphide solution (p. 95) only a very small bubble of gas (probably argon) remained.

The presence of oxygen in nitric acid is readily demonstrated by pouring a little of the acid down the red-hot stem of a clay

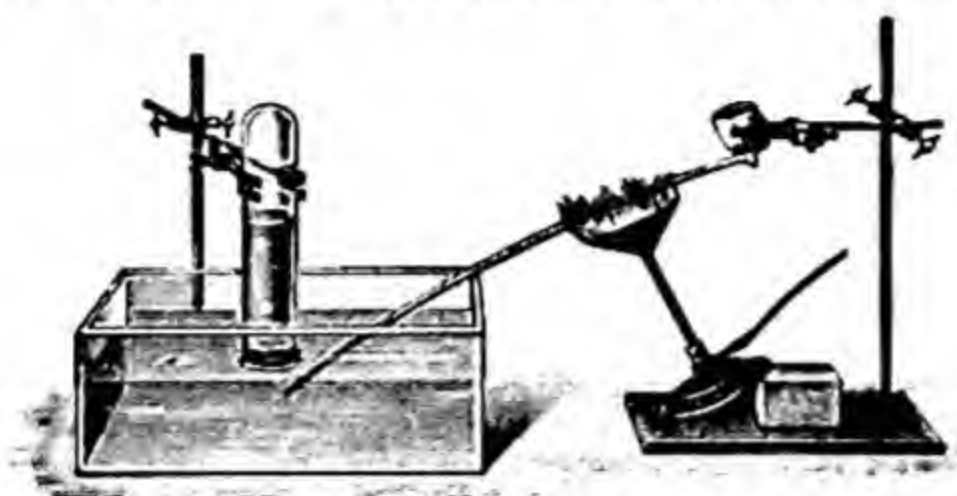
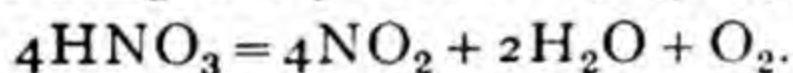


FIG. 256.—DECOMPOSITION OF NITRIC ACID BY HEAT.

tobacco pipe, and collecting the bubbles of oxygen over water which absorbs the  $\text{NO}_2$  also produced (Fig. 256) :



**Preparation of nitric acid.**—Nitric acid is prepared in the laboratory by distilling a mixture of potassium or sodium nitrate

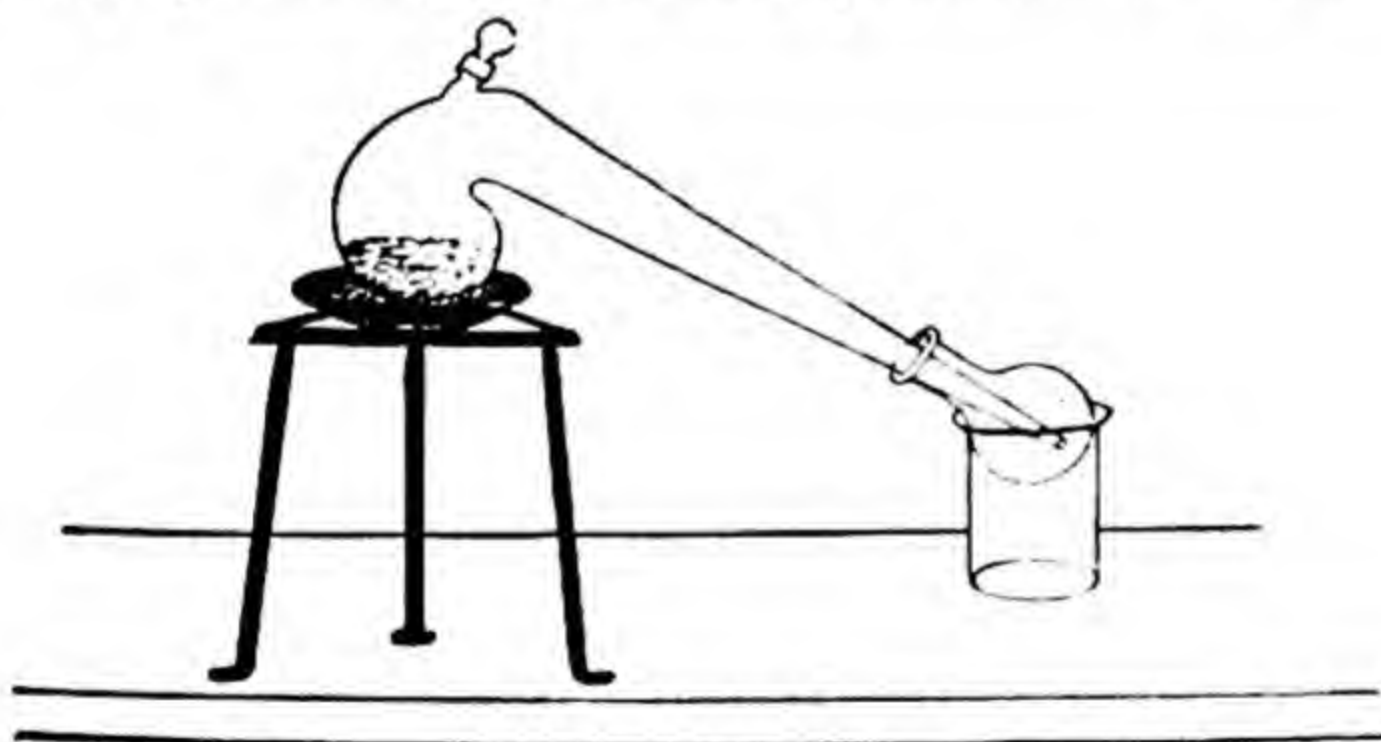
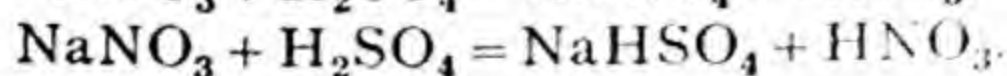
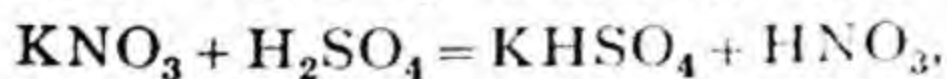
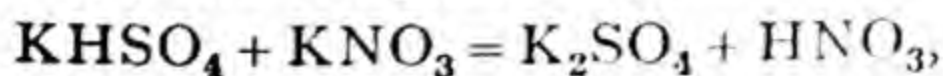


FIG. 257.—PREPARATION OF NITRIC ACID IN THE LABORATORY.

with concentrated sulphuric acid in a glass retort, and collecting the acid in a receiver cooled by water (Fig. 257). The reactions are :

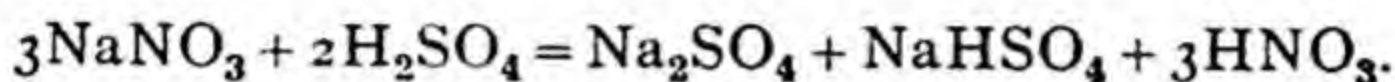


With excess of nitre and a higher temperature a further reaction occurs :



but a glass retort would crack at the temperature required, and much of the acid would be decomposed (see above).

On the technical scale the distillation is carried out in large cast-iron retorts, and the nitric acid is condensed in stoneware or acid-resisting metal (silicon-iron) pipes cooled by water. Such proportions of sodium nitrate and sulphuric acid are used as will give a residue containing equimolecular amounts of acid and normal sodium sulphates, since this is fusible and can be run out of the retort :



The oxides of nitrogen formed by the decomposition of the acid are absorbed in a tower with water (Fig. 258). Any nitrogen

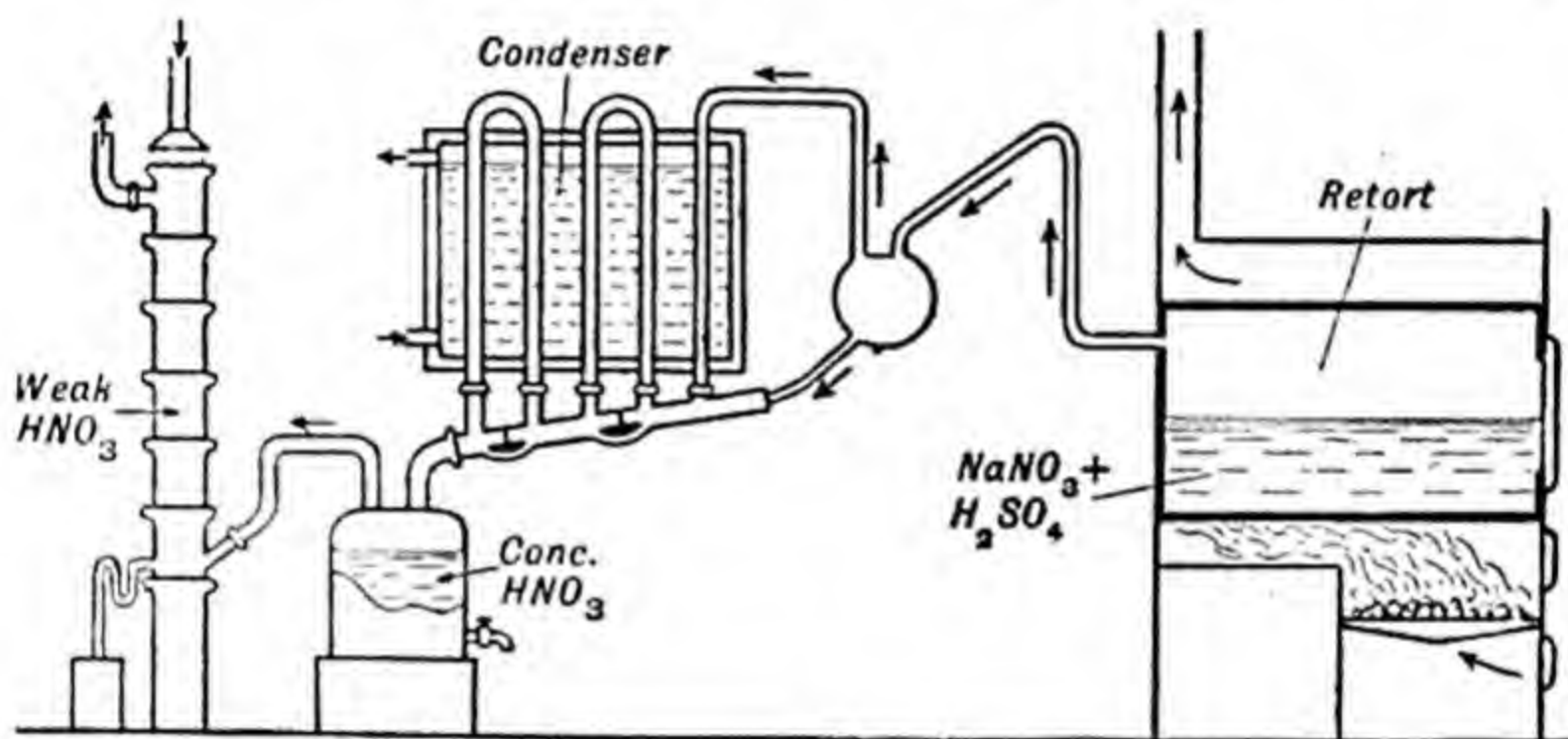
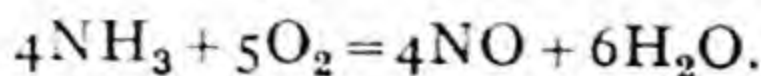


FIG. 258.—MANUFACTURE OF NITRIC ACID BY DISTILLING SODIUM NITRATE WITH SULPHURIC ACID.

peroxide dissolved in the acid, colouring it yellow, may be removed by a stream of dry air.

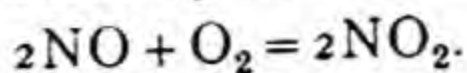
Nitric acid is now usually made by the catalytic oxidation of ammonia, which may be synthesised from nitrogen and hydrogen (p. 378). The arc process is now no longer used.

**The oxidation of ammonia.**—In 1788, the Rev. Isaac Milner, President of Queens' College, Cambridge, found that ammonia, when passed over heated manganese dioxide, is oxidised to red fumes which on dissolving in water form nitric acid. The French chemist Kuhlmann, in 1839, found that ammonia can be oxidised by passing it, mixed with air, over heated platinum (see p. 381), which acts as a catalyst :





The colourless gas, on cooling, becomes red from further oxidation of the nitric oxide by the excess of oxygen :



It may be absorbed in water, with formation of nitric acid, as described under the arc process.

The process was used in France during the Napoleonic wars, and on a gigantic scale in Germany during the Great War. It is also used to supply oxides of nitrogen to sulphuric acid chambers (p. 361). On the large scale the mixture of ammonia

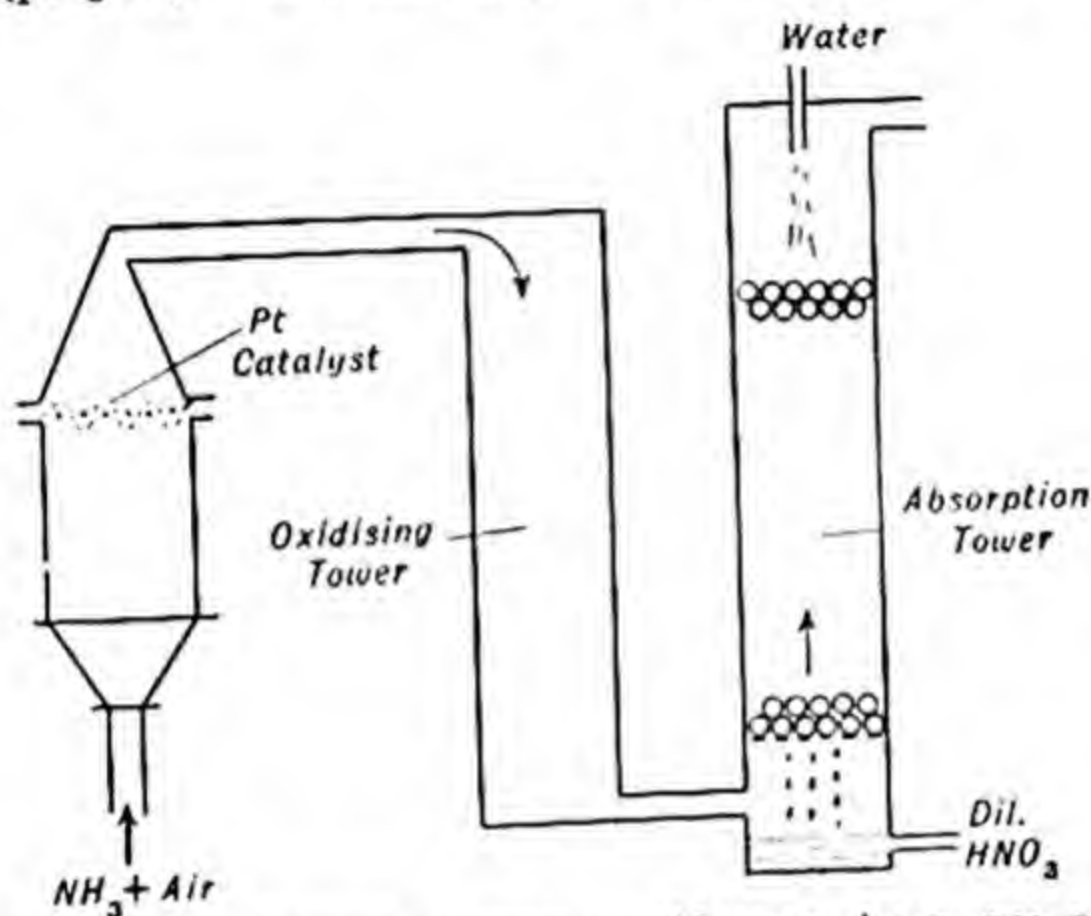


FIG. 259.—MANUFACTURE OF NITRIC ACID BY THE OXIDATION OF AMMONIA.

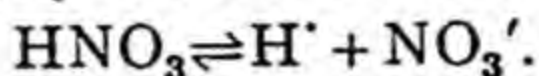
gas (1 vol.) and air (7.5 vols. or more) is preheated and passed through heated flat platinum gauzes (Fig. 259), or through heated granules of a catalyst made from iron oxide and oxides of other metals, such as bismuth, which act as promoters and increase the catalytic activity of the iron oxide.

**Properties of nitric acid.**—Nitric acid when pure is a colourless, strongly fuming, and highly corrosive liquid. Great care must be exercised in handling the concentrated acid. It attacks the skin violently, staining it bright yellow, and if spilled on the clothes it corrodes them so quickly that nothing can usually be done to save them. The vapour is poisonous.

The acid is usually coloured more or less yellow owing to decomposition with formation of nitrogen peroxide (p. 387). This decomposition occurs when the *vapour* of the acid is exposed to light, as in a partly filled bottle. The *liquid* acid does not

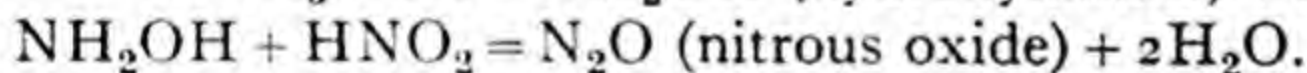
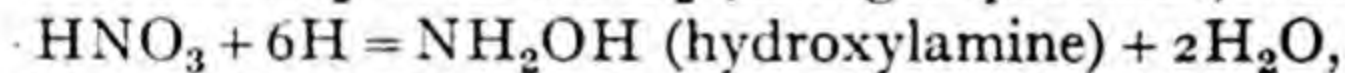
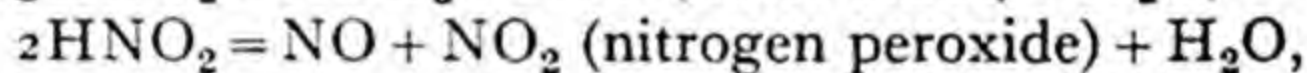
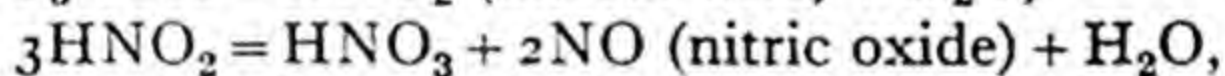
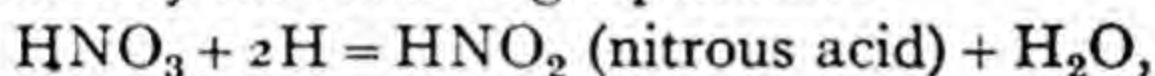
undergo decomposition. A yellow, so-called *fuming nitric acid* is prepared by adding a little starch to the nitrate and sulphuric acid in the distillation : part of the nitric acid is then reduced.

Nitric acid mixes readily with water, forming a strongly acid liquid, since it is largely ionised in solution, and is, therefore, a strong acid :



It is monobasic, since it contains only one atom of hydrogen which can be replaced by metals, and forms only one series of salts, the *nitrates*. These are obtained by the action of nitric acid on the metals, oxides, hydroxides, or carbonates. It is important to remember that in *the action of nitric acid on metals*, hydrogen is *not* evolved except with very dilute nitric acid and magnesium, but oxides of nitrogen are formed by the reduction of the acid.

The production of oxides of nitrogen by reduction of the nitric acid by the hypothetical nascent hydrogen can be represented by the following equations :

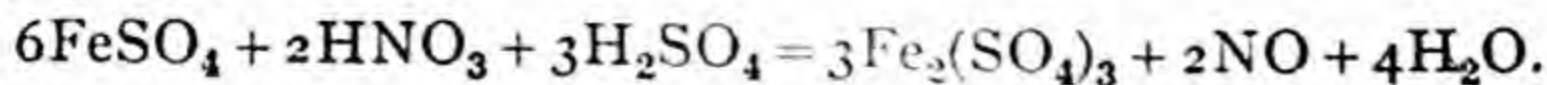


According to another theory, the nitric acid reacts with metals only when it contains nitrous acid.

If the yellow nitric acid containing nitrogen peroxide, freshly distilled from nitre and sulphuric acid, is poured upon copper, it does not usually act upon it, but when a little water is added the copper is at once dissolved.

Nitric acid acts as an *oxidising agent*: iodine, phosphorus and sulphur with the concentrated acid are oxidised to iodic acid, phosphorous and phosphoric acids, and sulphuric acid; the nitric acid is reduced and oxides of nitrogen are evolved. Tin is violently oxidised by the concentrated acid to hydrated stannic oxide; glowing charcoal burns brilliantly in concentrated nitric acid; heated sawdust is inflamed by the acid.

Ferrous salts reduce nitric acid to nitric oxide, NO, and this dissolves in the excess of ferrous salt to form a black solution, from which nitric oxide is expelled on heating. The first reaction is :





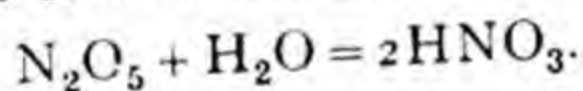
In the case of nitrates, concentrated sulphuric acid must be added before the colour appears.

The reaction is applied in the **brown-ring test** for nitrates. A few crystals of ferrous sulphate are dissolved in a cold solution of the nitrate in a test-tube, and pure concentrated sulphuric acid is cautiously poured into the liquid so as to form a distinct heavy layer below. At the junction of the two liquids a black, brown, or (with traces only of nitrate) purple, ring appears (Fig. 260). On shaking, the liquid becomes hot, owing to admixture of the sulphuric acid and water, and the colour disappears, owing to expulsion of the nitric oxide from the unstable compound with ferrous sulphate.



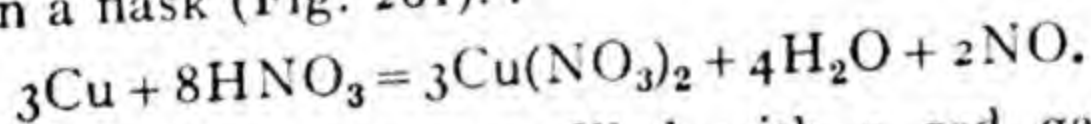
FIG. 260.—  
THE BROWN-  
RING TEST FOR  
NITRATES.

**Nitrogen pentoxide.**—This oxide, called **nitric anhydride**, is obtained by dehydrating cold, concentrated nitric acid with phosphorus pentoxide, distilling by gently heating, and condensing the white crystals of nitrogen pentoxide in a freezing mixture. It is unstable, is an oxidising agent, and dissolves in water to form nitric acid :



**Nitric oxide.**—Although nitric oxide appears to have been obtained by Van Helmont, and was certainly prepared by Mayow and by Hales, it was first recognised as a distinct gas by Priestley in 1772 ; he named it *nitrous air*.

Nitric oxide is prepared by the action of *diluted* nitric acid (1 vol. of concentrated acid and 1 vol. of water) on copper turnings in a flask (Fig. 261). :



The flask at first becomes filled with a red gas, due to the oxidation of the nitric oxide by the atmospheric oxygen in the apparatus. When this has been swept out the gas becomes nearly colourless, and the nitric oxide then collected in jars over water is quite colourless, since any trace of nitrogen peroxide dissolves in the water. The gas so obtained is not quite pure, and in the later stages of the reaction may contain nitrogen or nitrous oxide. The first portions of gas should, therefore, be collected for experiments. If the gas is first absorbed in cold ferrous sulphate solution (forming a black liquid), and then expelled again by heating, it is nearly pure.

**Properties of nitric oxide.**—Nitric oxide is a colourless gas, slightly heavier than air and only sparingly soluble in water.

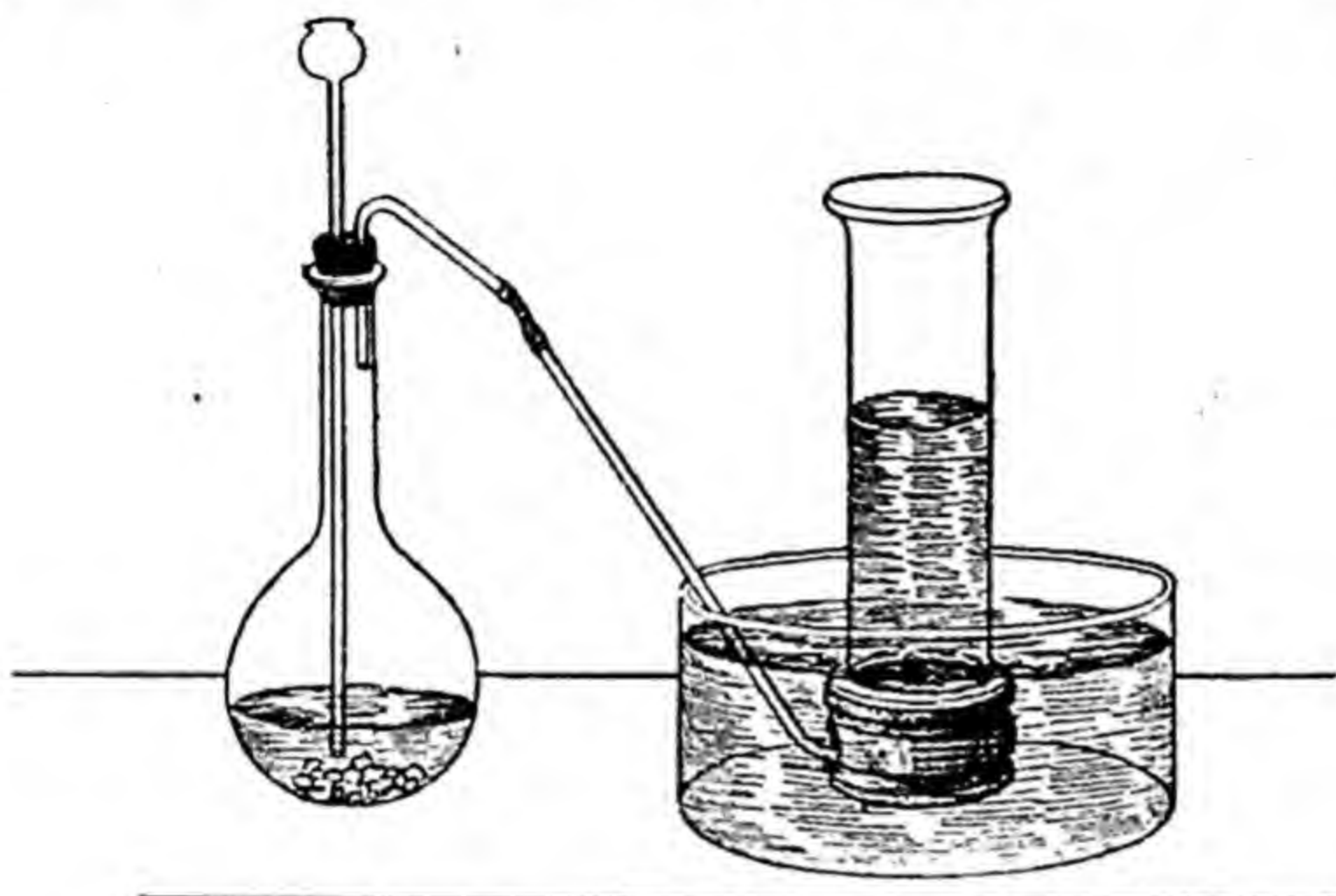
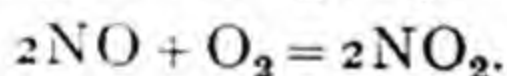
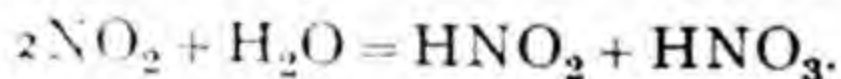


FIG. 261.—PREPARATION OF NITRIC OXIDE FROM COPPER AND DILUTE NITRIC ACID.

It combines readily with free oxygen, *e.g.*, on mixing with air, to form a brownish-red gas, nitrogen peroxide :



When mixed with air or oxygen *over water*, the nitrogen peroxide first formed is absorbed by water to form nitrous and nitric acids :

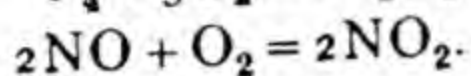
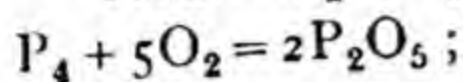
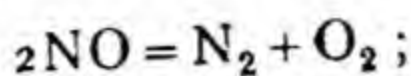


Priestley, who carried out this reaction, says : ‘ I hardly know any experiment that is more adapted to amaze and surprize than this is, which exhibits a quantity of air, which, as it were, devours a quantity of another air half as large as itself, and yet is so far from gaining any addition to its bulk, that it is considerably diminished by it.’

Some combustible substances burn in nitric oxide, but the material must first be ignited in air, and then introduced, freely burning, into the nitric oxide. The latter is the most stable oxide of nitrogen : it begins to decompose into nitrogen and oxygen appreciably only above  $1000^\circ$ , and unless this temperature is attained combustion does not proceed. The substances

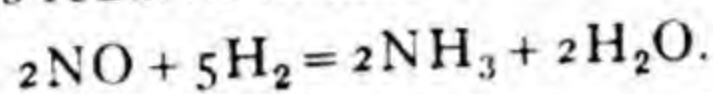


burn in the oxygen liberated by the thermal decomposition of the gas. A lighted taper, burning sulphur, and charcoal are extinguished in the gas. Feebly burning phosphorus is also extinguished, but if burning brightly the combustion continues brilliantly, red fumes being produced as well as white clouds of phosphorus pentoxide :



A mixture of carbon disulphide vapour and nitric oxide burns with a brilliant blue flame.

A mixture of hydrogen and nitric oxide when passed over heated platinum is reduced to ammonia :



The composition of nitric oxide is determined by heating a piece of potassium in the gas confined over mercury in a bent hard glass tube (Fig. 262). The oxygen combines with the potassium ; on cooling, the residual nitrogen occupies *half* the volume of the nitric oxide. The vapour density of nitric oxide is 15 ( $\text{H} = 1$ ), hence the molecular weight is 30. This contains half its volume, or half a molecule, viz. 14 parts of nitrogen, *i.e.*, 1 atom of nitrogen, and hence  $30 - 14 = 16$  parts, or 1 atom of oxygen. Thus the formula is  $\text{NO}$ . (Nitric oxide will *not* explode with hydrogen and the composition cannot be found in this way ; see Nitrous Oxide.)

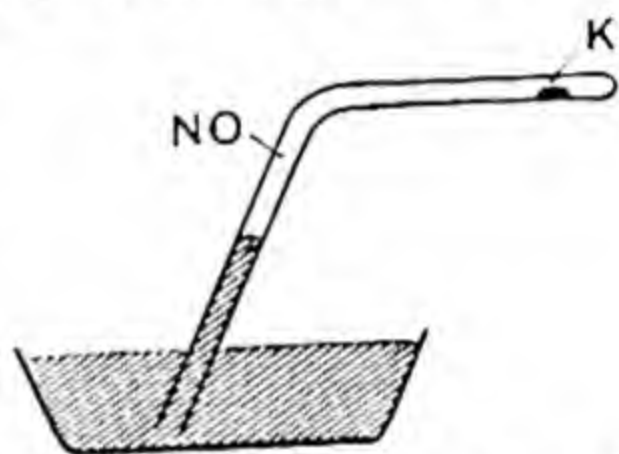
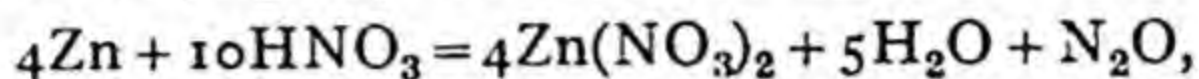


FIG. 262.—COMPOSITION OF NITRIC OXIDE

**Nitrous oxide.**—The most familiar oxide of nitrogen in everyday life is **nitrous oxide**,  $\text{N}_2\text{O}$ , known as laughing gas and used by dentists in producing insensibility during minor operations. Nitrous oxide was discovered by Priestley in 1772. He allowed 'nitrous air' (nitric oxide) to stand in contact with moist iron filings or liver of sulphur. This treatment of the gas, he says : 'makes it not only to admit a candle to burn in it, but enables it to burn with an *enlarged flame*, by another flame (extending every where to an equal distance from that of the candle, and often plainly distinguishable from it) adhering to it.' Priestley also obtained the gas by dissolving iron and zinc in diluted nitric acid : he called it *dephlogisticated nitrous air*.

The peculiar gas was carefully examined by Humphry Davy in 1799. He prepared it pure by heating ammonium nitrate, called it *nitrous oxide*, determined its composition, and discovered its narcotic physiological action, sometimes preceded by the exhilarating effects which led to the name laughing gas.

**Preparation of nitrous oxide.**—Nitrous oxide is *formed* in certain cases by the reduction of nitric oxide (see above), or of dilute nitric acid, *e.g.*, by the action of zinc :



but it is never *prepared* by these methods. It has recently been obtained directly from oxygen and nitrogen, but only by a very special method.

In the preparation of the gas, dry ammonium nitrate is decomposed by careful heating (below  $200^\circ$ ) in a glass flask or retort (Fig. 263). Care must be taken that the salt is not overheated,

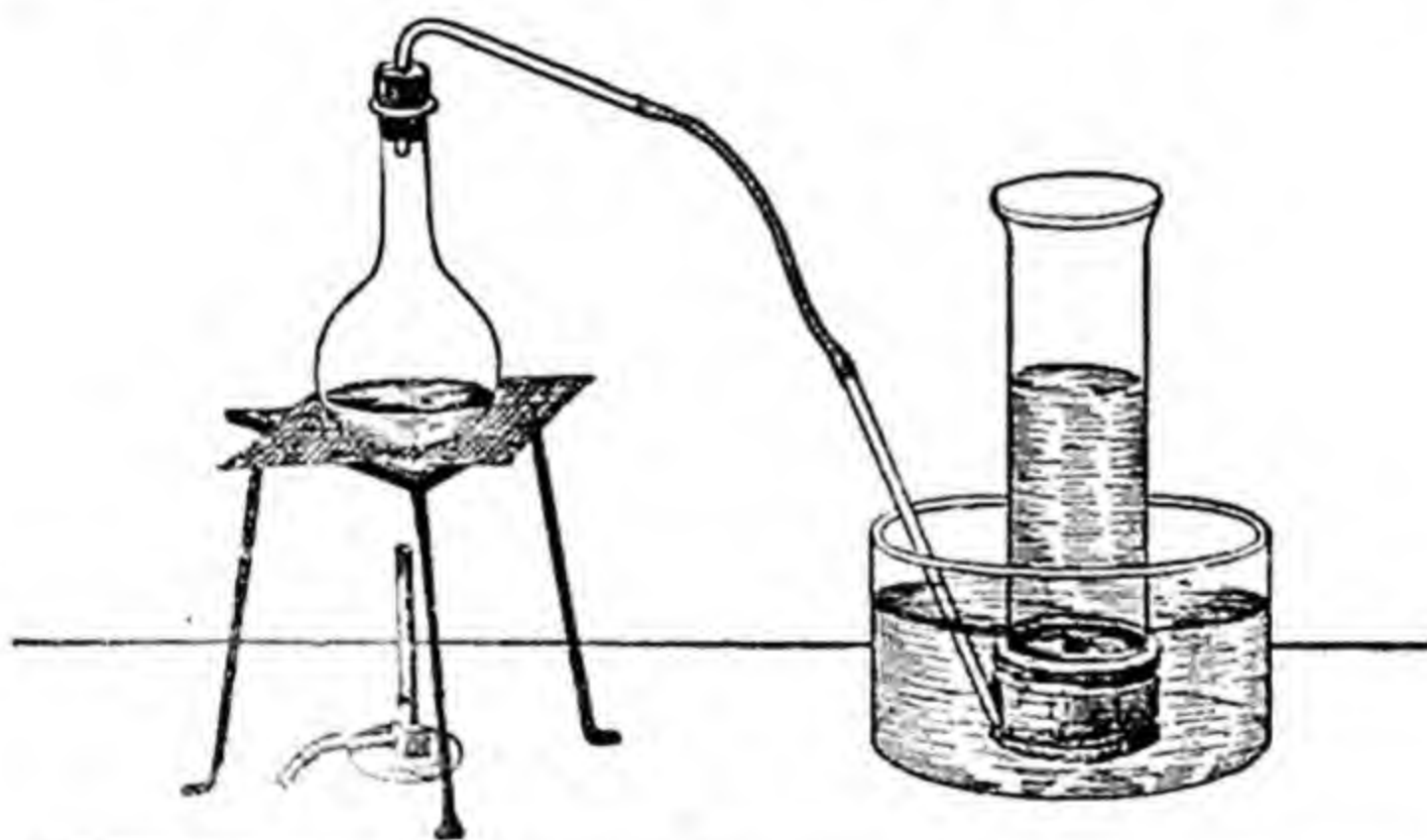
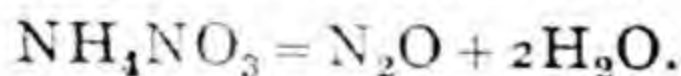


FIG. 263. —PREPARATION OF NITROUS OXIDE BY HEATING AMMONIUM NITRATE.

otherwise explosion of the ammonium nitrate may occur. The salt decomposes into nitrous oxide and water :



The gas is collected over hot water, since it is appreciably soluble in cold water.

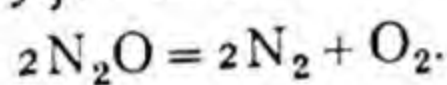
Nitrous oxide prepared from ammonium nitrate on the large scale is carefully purified, and liquefied by compression into steel



cylinders. It is used as an anaesthetic in minor operations, *e.g.*, in dentistry, and is produced by the evaporation of the liquid in the cylinders. It must be free from other oxides of nitrogen, since these are poisonous.

**Properties of nitrous oxide.**—Nitrous oxide is a colourless gas, heavier than air, with a faint sweetish odour and taste. It is fairly soluble in water and more soluble in alcohol.

Nitrous oxide supports combustion more vigorously than air, since it yields on decomposition a gas containing *one-third* its volume of oxygen, as compared with *one-fifth* in air :



(Nitric oxide gives a gas containing *half* its volume of oxygen, but does not support combustion so easily as air or nitrous oxide. This arises from the circumstance that nitrous oxide is much more easily decomposed by heat than nitric oxide. Combustion in nitric oxide, once it begins, is more vigorous than that in nitrous oxide.)

A taper burns brightly in the gas, and a glowing chip is re-kindled, exactly as in oxygen. Nitrous oxide is, however, *distinguished* from oxygen (i) by its smell ; (ii) by its greater solubility in water ; and (iii) by the fact that it does not give a red gas (nitrogen peroxide) when mixed with nitric oxide (see p. 396).

Feebly burning sulphur is extinguished by nitrous oxide, but when the sulphur is burning brightly its combustion continues with enhanced brilliancy. Phosphorus burns brilliantly :



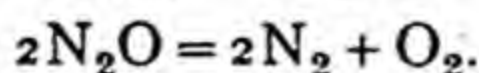
FIG. 264.

#### NITROUS OXIDE CYLINDERS AND BREATHING APPARATUS.

THE INHALER CONSISTS OF A FACE-PIECE OR MASK TO COVER THE MOUTH AND NOSE TO EXCLUDE ALL AIR. CONNECTED TO IT IS A TWO-WAY METAL TAP ATTACHED TO A RUBBER GAS BAG HAVING A SMALL SUPPLY TUBE LEADING TO THE TWO CYLINDERS CONTAINING A SUPPLY OF NITROUS OXIDE. THE TWO-WAY TAP HAS TWO VALVES PLACED IN IT WHICH ALLOW GAS TO PASS INTO THE FACE-PIECE, AND OUT FROM IT TO THE SURROUNDING AIR. THE DISCHARGE OF THE GAS IS CONTROLLED BY THE FOOT PLATE SEEN ON ONE OF THE CYLINDER VALVES, WHICH WHEN TURNED TO THE LEFT, PERMITS GAS TO PASS THROUGH THE RUBBER SUPPLY TUBE TO THE GAS BAG.

sodium, potassium, and iron wire burn in the gas as in oxygen. A hydrogen flame introduced into nitrous oxide becomes greatly enlarged.

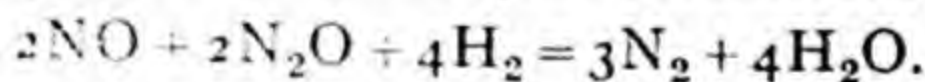
In all cases the combustible unites with the oxygen of the nitrous oxide, whilst the nitrogen of the gas is set free. Nitrous oxide is an endothermic compound (p. 284) and is decomposed by shock, *e.g.*, by exploding it together with electrolytic gas:



Davy determined the composition of nitrous oxide by heating potassium in a measured volume of the gas confined in a bent tube over mercury (cf. p. 393). After cooling, an equal volume of nitrogen remained. Thus, *nitrous oxide contains its own volume of nitrogen*. The relative density of the gas is 22, hence the molecular weight is 44. But this contains a molecular weight (*i.e.*, an equal volume) of nitrogen,  $\text{N}_2$ , of weight 28, and therefore  $44 - 28 = 16$  parts, or one atom of oxygen. The formula is therefore  $\text{N}_2\text{O}$ .

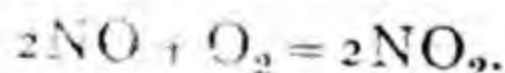
The formula may also be established by exploding the gas with hydrogen in a eudiometer. If 20 c.c. of nitrous oxide are mixed with 20 c.c. of hydrogen and exploded, 20 c.c. of nitrogen are left. The hydrogen must have combined with 10 c.c. of oxygen to form liquid water, so that 2 vols. of nitrogen are combined in 2 vols. of nitrous oxide with 1 vol. of oxygen, and the formula is  $\text{N}_2\text{O}$ .

Nitric oxide does *not* explode with hydrogen, but if mixed with an equal volume of nitrous oxide both gases explode when the mixture is sparked with an equal volume of hydrogen:

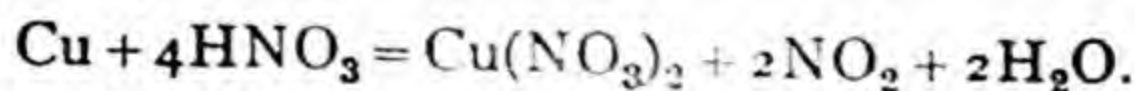


If the composition of one gas (*e.g.*,  $\text{N}_2\text{O}$ ) is known, that of the other may be found by this experiment.

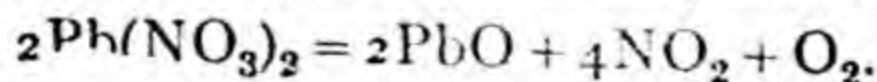
**Nitrogen dioxide (or peroxide); nitrogen tetroxide.**—The brownish-red gas formed by the direct combination of nitric oxide with oxygen is nitrogen dioxide:



It is produced by the action of *concentrated* nitric acid on copper (Priestley):



It is more easily obtained by the decomposition of lead nitrate by heat:





The dry powdered lead nitrate is heated in a hard glass tube, and the gas passed through a U-tube cooled in a mixture of ice and salt (Fig. 265). A yellow *liquid* collects in the cooled tube. A glowing chip held over the exit of the U-tube bursts into flame, showing that oxygen is also evolved.

Nitrogen peroxide is really a *liquid* substance at room temperature, but it is so volatile that the vapour is readily produced. It is very poisonous and should not be inhaled.

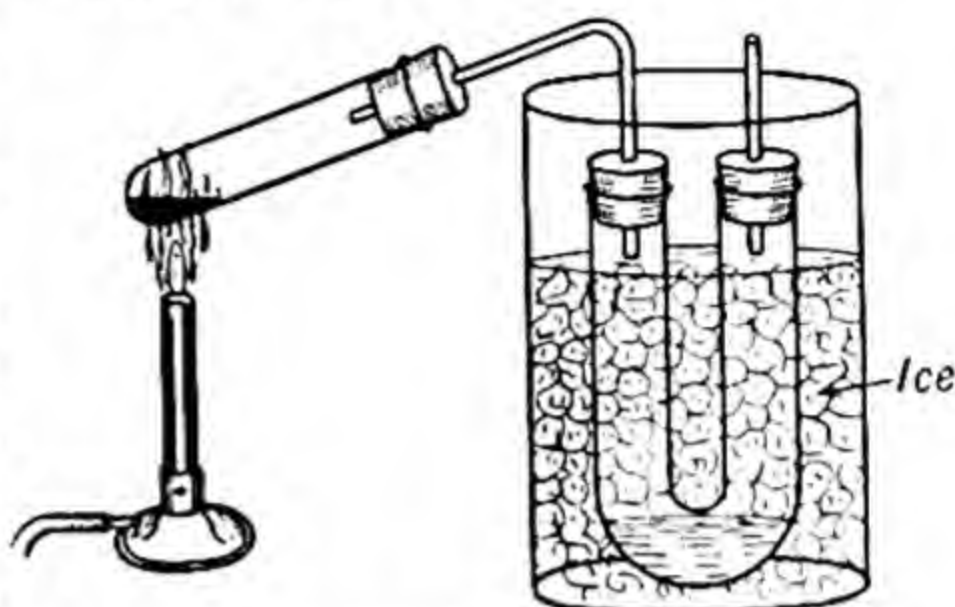
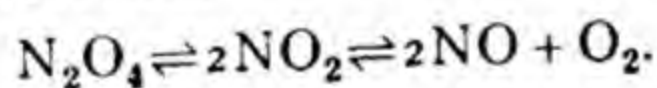


FIG. 265.—PREPARATION OF NITROGEN PEROXIDE BY HEATING LEAD NITRATE.

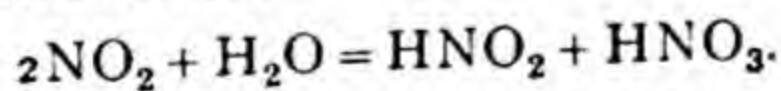
When cooled to  $-9.04^{\circ}$  nitrogen peroxide forms a pale yellow *solid*; the liquid becomes darker coloured on heating and boils at  $26^{\circ}$  yielding a red *vapour*, the density of which shows that it is largely  $\text{N}_2\text{O}_4$ , although some  $\text{NO}_2$  is present. The vapour density becomes smaller, and the colour of the gas darker, on further heating. At  $140^{\circ}$  the density shows that the gas consists solely of  $\text{NO}_2$ .

On strong heating, the  $\text{NO}_2$  decomposes into nitric oxide and oxygen, and the gas becomes colourless. On cooling, all the above changes are reversed.

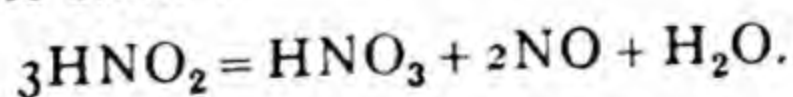


Nitrogen peroxide does not easily support the combustion of a taper, but brightly burning sulphur and phosphorus burn in the gas.

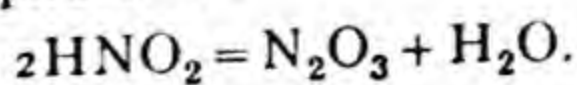
Nitrogen peroxide is absorbed by water forming a mixture of nitrous and nitric acids:



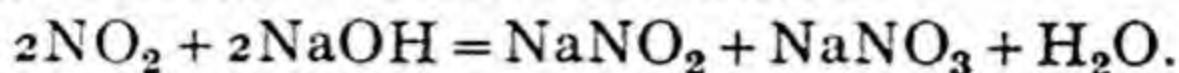
Nitrous acid is unstable and much of it decomposes with evolution of nitric oxide:



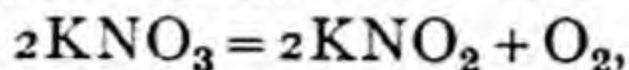
Some of the nitrous acid decomposes into **nitrogen trioxide**, which colours the liquid blue:



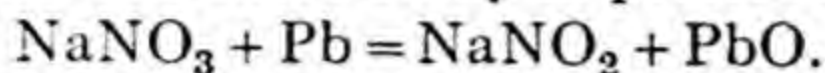
Nitrogen peroxide is absorbed by alkalies forming a mixture of equimolecular amounts of *nitrite* and *nitrate* :



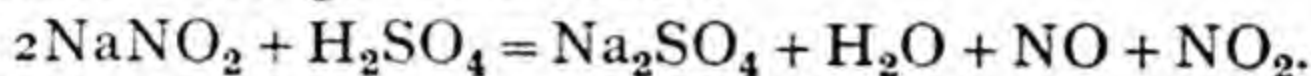
Sodium and potassium nitrites are obtained by heating the nitrates :



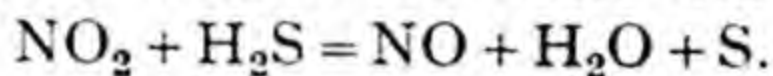
a reaction which occurs more easily in presence of lead :



They evolve a red gas with acids :



Nitrogen peroxide is reduced to nitric oxide by hydrogen sulphide :



#### \*THE INERT GASES.

In 1894 the late Lord Rayleigh found that the density of nitrogen gas prepared from the atmosphere was slightly greater than that obtained from ammonium nitrite or other chemical compounds containing the element. He remarked that Cavendish in 1785 had noticed a small uncombined residue when air was sparked with oxygen over potash solution (p. 386), and suspected that atmospheric nitrogen might contain a small amount of a heavier gas, which does not combine with other elements to form compounds and is therefore not present in nitrogen compounds. In conjunction with Sir William Ramsay he succeeded in removing the true nitrogen from atmospheric nitrogen by sparking it with oxygen over an alkali, and also by passing it repeatedly over strongly heated magnesium, which combines with nitrogen to form magnesium nitride.

About one per cent. of the atmospheric nitrogen was so found to consist of a new gas, to which the name **argon**, derived from a Greek word meaning inert, was given. It was found to be completely inactive chemically, it does not form any compounds, even with itself, so that its molecules are really single atoms, and the atomic weight is equal to the molecular weight, about 40. Argon is now obtained technically from *liquid oxygen* from the air, which contains about three per cent. of argon (p. 278). It is used in filling the best kinds of electric lamps. 'Gas-filled' lamps are generally filled with nitrogen. The tungsten filament in a gas-filled lamp may be run at a higher temperature than in a vacuum lamp without causing the glass bulb to become blackened by volatilised metal.



In 1868 Lockyer and Janssen observed independently that the layer of the sun's atmosphere from which flames or prominences are erupted gave a spectrum of bright lines, mostly due to hydrogen. There was, however, a strong yellow line which could not be so identified, and after full investigation, Lockyer

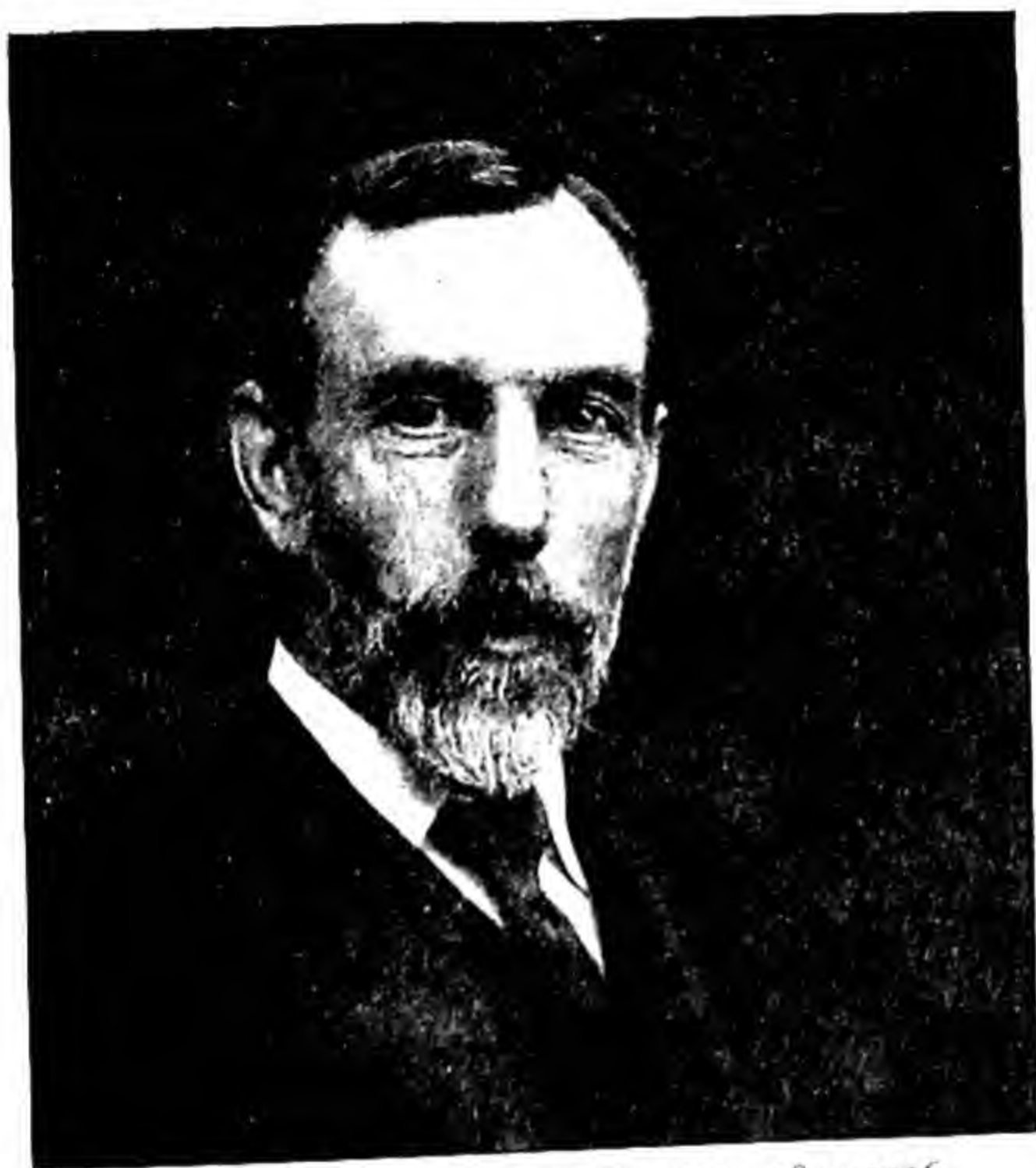


FIG. 266.—SIR WILLIAM RAMSAY, 1852-1916.

came to the conclusion that the line was the hallmark of a new element in the sun. To this unknown element he gave the name **helium**, from the Greek *helios*, the sun. Ramsay, soon after the discovery of argon, detected this element in the gas evolved on heating certain rare minerals, e.g., cleveite. Helium exists only in *very* minute traces in the atmosphere, but it occurs in larger amounts (as much as one per cent.) in the natural gas in some parts of America and Canada, and in the gas from some French mineral springs. It has the lowest boiling point ( $-269^{\circ}\text{C.}$ ) of any substance known,



11 MM. DIAMETER, 900 VOLTS, AND 25 MILLIAMPERES. AS MANUFACTURED BY NEON LIGHTS (1923) LTD., AT HOUNSLOW.

so that it can be separated by liquefying the other gases present with it. Helium, like argon, is completely inert, and since it is only twice as heavy as hydrogen ( $H_2 = 2$ ;  $He = 4$ ) it has been used to a limited extent in filling airships in America, where large stocks of the gas are available, since the danger of fire and explosion is thus eliminated.

Ramsay and Travers also discovered three other inert gases in the atmosphere: **neon**, **krypton**, and **xenon**. Neon exists to the extent of about 15 vols. in 1,000,000 vols. of air, and is extracted and used for filling the electric lamp tubes used for giving the striking orange-red light in advertising and, since yellow or orange light penetrates fog much more easily than white light, neon lamps are used in fogs (Fig. 267). They were used at Lympne aerodrome, on the London-Paris air route. Sixteen neon tubes, each 20 feet long, were used, giving a total candle power of 6000. There was a gigantic neon lamp in the ground at the British Empire Exhibition at Wembley. Neon is also used in sparking plug testers. Krypton and xenon are present in air in very minute amounts: it has been said that if the molecules of air could be seen, and were to pass before the eye at the rate of one every second, an argon molecule would be seen every two minutes, a krypton molecule once every eight months, and a xenon molecule once every five or six years.

An interesting use for helium has been proposed. Men working in compressed air, as in caissons under water in tunnel construction, often collapse

FIG. 267.—NEON ELECTRIC TUBULAR LAMP.



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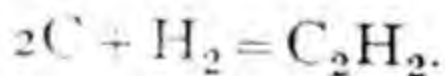
when brought too quickly into air at ordinary pressure. This is due to the nitrogen of the air dissolving under pressure in the blood, tissues, and even the spinal cord. When the pressure is released, this nitrogen is liberated in bubbles which may destroy the spinal cord, affect the brain, interfere with the action of the lungs, and even cause death. This limits the depths to which divers may safely descend. Helium is much less soluble than nitrogen and diffuses more rapidly, so that if a mixture of oxygen and helium were supplied under pressure instead of ordinary air, practically no gas bubbles would be liberated when the pressure was reduced.

## CHAPTER XXIII

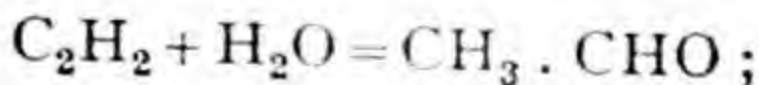
### CARBON

**The chemistry of carbon.**—Perhaps no other element is so important in everyday life as carbon and certainly none forms so many compounds. More than 200,000 carbon compounds have been described and the number is constantly increasing. The study of carbon compounds, many of which are of no particular interest, forms a special branch of chemistry, which is still called **organic chemistry**, because living plants and animals are largely composed of carbon compounds and it was formerly supposed that, with the exception of a few simple ones, these compounds could be formed only by the agency of vegetable or animal life, or the 'vital force.' This artificial barrier between compounds of carbon and those of other elements was broken down when it was shown, in the nineteenth century, that many carbon compounds occurring in plants and animals could be *synthesised*, i.e., prepared from their elements, although a number of the more complex of them have still not been obtained in the laboratory. These syntheses, of course, bring us no nearer to an understanding of 'life,' since no organic compound as such ever shows the slightest trace of vitality; not even the complicated organic compounds obtained from plants and animals.

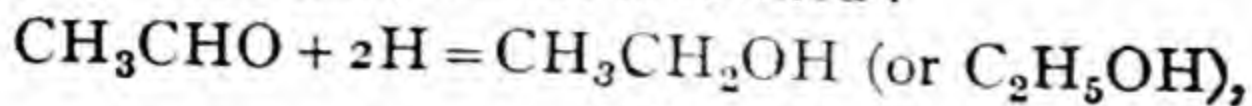
By burning an electric arc between carbon poles in hydrogen, **acetylene**,  $C_2H_2$ , is formed :



This can be made to add on the elements of water to form **acetaldehyde**,  $CH_3 \cdot CHO$  :

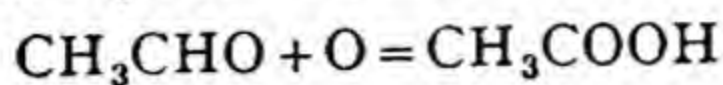


from this, by reduction, **alcohol** is formed :



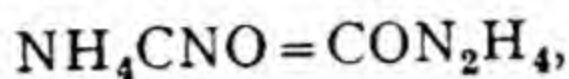


whilst by oxidation it yields acetic acid :



From alcohol and acetic acid numerous derivatives can be formed, and in this way an ever lengthening chain of carbon compounds may be built up from the elements.

The production of urea by heating ammonium cyanate :



carried out by Wöhler in 1828, is usually said to have removed the distinction between inorganic and organic compounds, but ammonium cyanate could not then be regarded as an inorganic substance, and the interest of Wöhler's discovery was that it provided an example of isomerism (p. 126), ammonium cyanate and urea having the same composition.

The element carbon itself exists in *allotropic forms*, and of one of these (the so-called amorphous carbon) there are several varieties :

- (1) Diamond.
- (2) Graphite (*plumbago* ; *black lead*).
- (3) 'Amorphous' carbon (*charcoal*, etc.).

The X-rays show (p. 189) that the so-called amorphous carbons, although having no external crystalline form, really contain sub-microscopic crystals of graphite, so that there are only two allotropic forms of carbon.

Diamond and graphite occur as minerals ; anthracite coal is a mineral form of amorphous carbon. Compounds of carbon and hydrogen, called hydrocarbons, are very numerous and mixtures of them are found in petroleum and in bituminous coal (which also contains some oxygen and nitrogen). Carbon dioxide,  $\text{CO}_2$ , occurs both uncombined and in combination as carbonates, such as calcium carbonate,  $\text{CaCO}_3$  (*chalk*, *limestone*, and *marble*), and magnesium carbonate,  $\text{MgCO}_3$ , and a compound of calcium and magnesium carbonates called *dolomite*. Combined and free carbon occur in cast iron and combined carbon in steel.

The bodies of plants and animals contain compounds of carbon with hydrogen and oxygen, and sometimes nitrogen, sulphur, and phosphorus. These so-called organic compounds comprise :

- (1) Carbohydrates, such as starch,  $\text{C}_6\text{H}_{10}\text{O}_5$  ; various sugars, such as glucose, or grape-sugar,  $\text{C}_6\text{H}_{12}\text{O}_6$ , and saccharose, or

cane-sugar,  $C_{12}H_{22}O_{11}$ ; and cellulose,  $C_6H_{10}O_5$ , or woody-fibre, all occurring in plants; (2) proteins, such as albumin, gelatin, and a number of very complicated compounds occurring both in plants and animals, which contain nitrogen, and usually sulphur and phosphorus, in addition to carbon, hydrogen, and oxygen.

**Diamond.**—The identity of the diamond with graphite and amorphous carbon (charcoal) was established by showing that

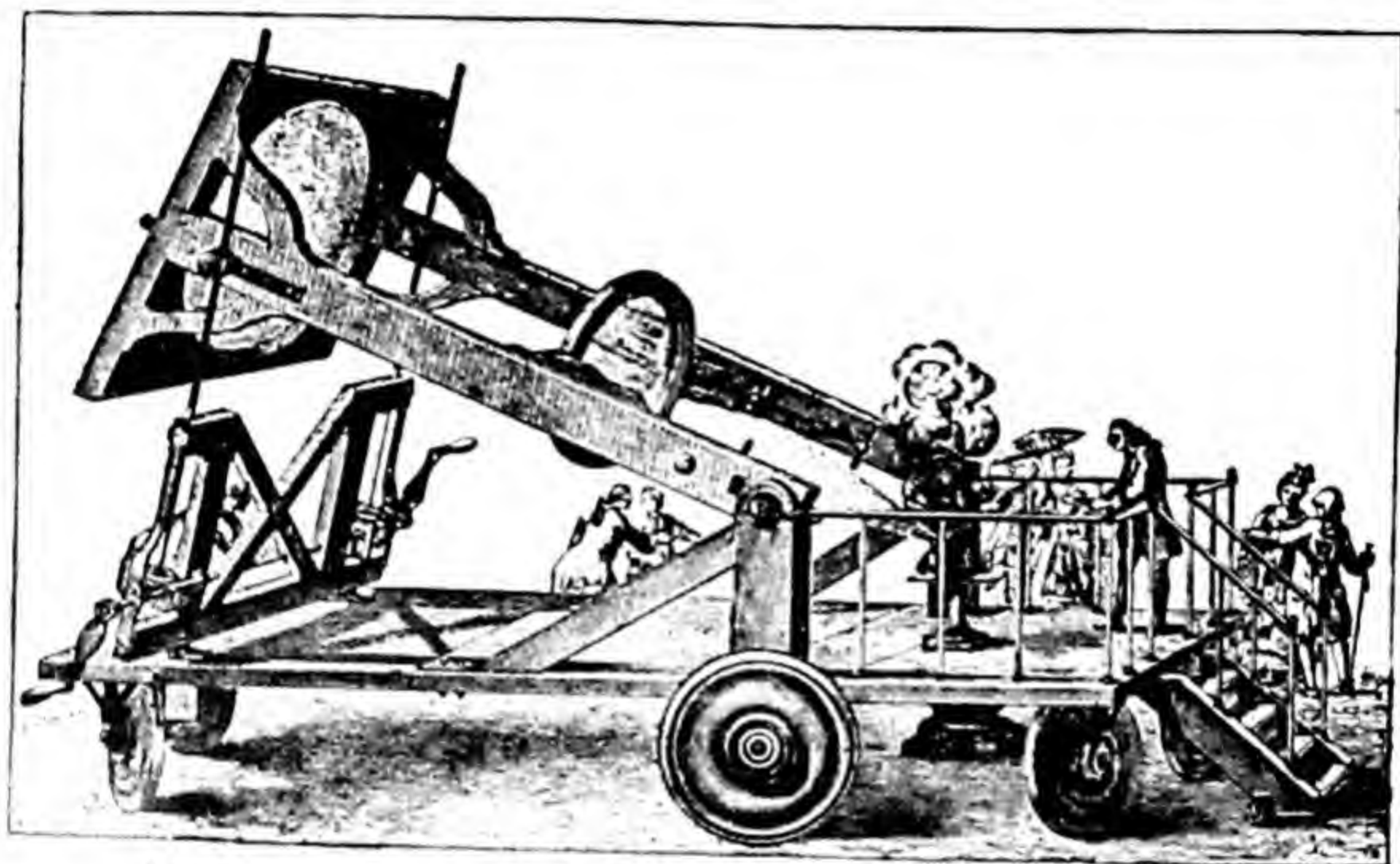


FIG. 278. LARGE BURNING GLASS USED BY LAVOISIER.

equal weights of the three, when burnt in oxygen, gave equal weights of the same product, carbon dioxide:



The combustibility of the diamond was foreshadowed by Newton, who, arguing from the similarity of its refractive index to those of oil of turpentine, camphor, and amber, suggested that it might be 'an unctuous [oily] substance coagulated.' The same might have been said of flint glass. The Florentine Academicians in 1694 heated a diamond in the focus of a powerful burning glass: it glowed like a red hot coal and disappeared. D'Arcet (1766) found that, when a diamond was strongly heated in a *closed* crucible, it remained unchanged. Davy and Faraday in 1814, using the original Florentine lens, burnt a diamond in oxygen. It took fire, and continued to burn, even if removed



from the focus, with a steady brilliant light. Nothing was produced but carbon dioxide, which rendered lime water milky. Smithson Tennant (1797) was able to burn diamonds by strongly heating them with fused nitre in a gold tube: he found that as much carbon dioxide was formed as Lavoisier had obtained from an equal weight of charcoal.

The combustion of the diamond in oxygen may be exhibited by heating a splinter of *carbonado* (black diamond) to whiteness by an electric current in a spiral of fine platinum wire supported by copper leads inside a jar of oxygen (Fig. 269). A little lime water shaken up with the gas afterwards is turned milky.

After many unsuccessful attempts to prepare diamonds artificially, the problem was to some extent solved by Moissan in 1893. He heated charcoal with iron in the electric furnace to a very high temperature. Fused iron dissolves carbon; on cooling the iron slowly most of the carbon deposits as graphite. When the iron is rapidly cooled, under ordinary conditions, the carbon remains in solid solution as the carbide,  $\text{Fe}_3\text{C}$ . Moissan cooled the white hot molten iron containing carbon suddenly by plunging the crucible, taken from the electric furnace, into cold water. The outer portion solidified at once, and the still liquid portion imprisoned within it solidified in due course. On dissolving away the iron with hydrochloric acid, a residue was left containing some microscopic diamonds, mostly black, but some transparent.

Colourless diamonds are almost chemically pure carbon: they are cut for gems by means of a revolving metal disc covered with diamond powder and oil. The diamond is exceedingly hard, and black diamonds (*carbonado* or *boart*) are used for rock-drills or, when crushed, for cutting and polishing clear diamonds. Diamond is very inert and resists the action of most chemical reagents. When strongly heated in air or oxygen, however, it burns away. Macquer in 1771 noticed that a burning diamond is surrounded by a small *flame*, showing that

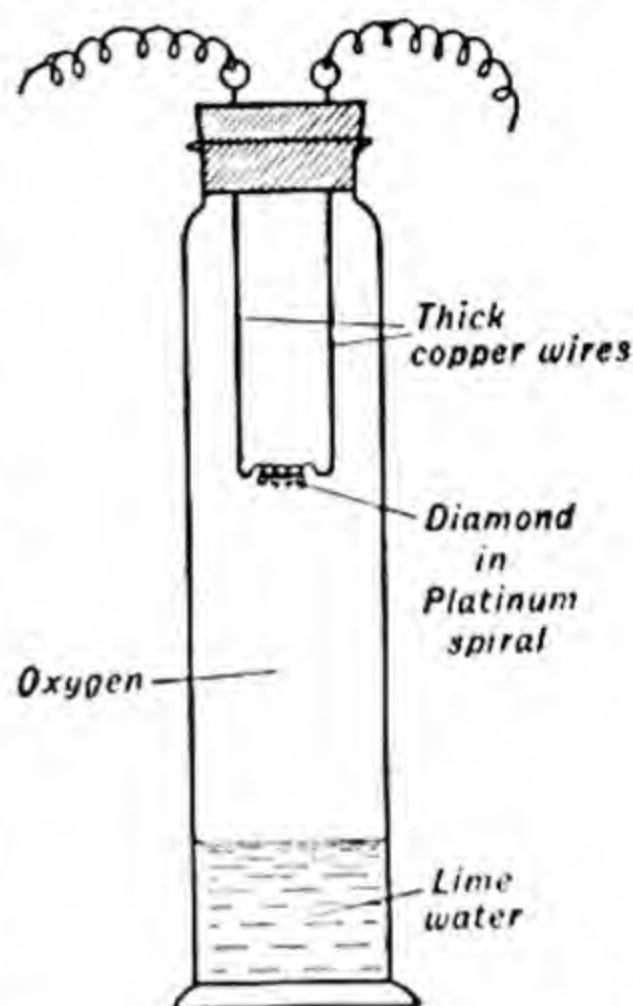


FIG. 269.—COMBUSTION OF THE DIAMOND IN OXYGEN.

gaseous carbon monoxide,  $\text{CO}$ , is formed and then burns to carbon dioxide.

**Graphite.**—Graphite (Greek *grapho*, I write), also called *plumbago* or *black lead*, is a soft mineral which marks paper and is used in making 'lead pencils' (which contain no

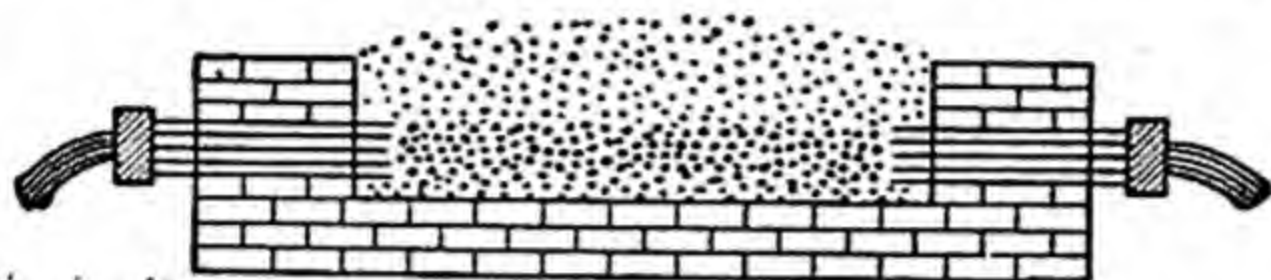


FIG. 270.—TECHNICAL PRODUCTION OF GRAPHITE IN THE ELECTRIC FURNACE.

metallic lead). It is also deposited from solutions of carbon in molten iron (see above), and is therefore sometimes found in blast furnaces in the form of *kish*. Graphite is obtained artificially by the Acheson process, in which a mixture of sand and powdered anthracite or coke is very strongly heated by an electric current passing through carbon rods embedded in the mass (Fig. 270). This *artificial graphite* is more expensive than natural graphite; it is very soft and pure and is used in suspensions in water (*aquadag*) or oil (*oildag*) as a lubricant.

Graphite, unlike other non-metals, is a good conductor of electricity. It burns only at a high temperature and, on account of its refractory character, is used in polishing iron which is exposed to heat and, mixed with clay, in making plumbago crucibles. Graphite is scarcely attacked by most

reagents but concentrated nitric acid slowly converts it into a curious substance containing carbon, hydrogen, and oxygen, called *graphitic acid*.

Graphite, like diamond, is crystalline, but the two crystalline forms are quite different.

By means of the X-rays, the arrangements of the atoms of carbon in diamond and graphite have been elucidated, and the results are shown in Figs. 271 and 272. It will be seen that each atom is joined to another by four valencies, but whereas the valencies are equally distributed in the diamond, in graphite

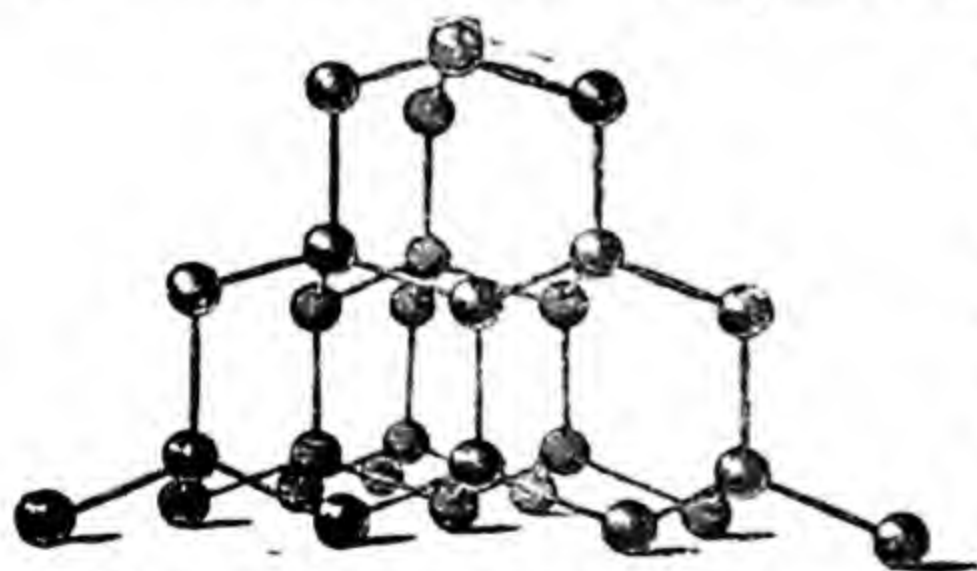


FIG. 271.—THE LINKING OF CARBON ATOMS IN THE DIAMOND.

atoms of carbon in diamond and graphite have been elucidated, and the results are shown in Figs. 271 and 272. It will be seen that each atom is joined to another by four valencies, but whereas the valencies are equally distributed in the diamond, in graphite



one of the valencies joins an atom with another in a plane at a greater distance. The hexagonal arrangement in graphite, and the tetrahedral arrangement in diamond, are clearly seen.

**'Amorphous' carbon.**—The following varieties of so-called amorphous carbon are usually described :

1. **Charcoal** : from wood, sugar, etc.
2. **Lampblack** : soot, gas black, acetylene black.
3. **Animal charcoal**, bone charcoal, ivory black.
4. **Coke** (coal, anthracite, etc.).
5. **Gas carbon**.
6. **Electrode carbon** : arc carbons, etc.

They are all black and opaque, the density and hardness depending largely on the temperature at which they were formed. Most varieties of charcoal are far from pure : the purest form is obtained by heating pure sugar in a closed crucible and then heating the resulting charcoal strongly in a current of chlorine to remove hydrogen.

Experiments with X-rays indicate that forms of so-called 'amorphous' carbon contain very minute crystals of graphite.

**Charcoal.**—There are several varieties of charcoal. **Wood charcoal**, used as fuel in countries where wood is abundant, is prepared by the **destructive distillation of wood**, *i.e.*, the decomposition of the latter by heat into volatile parts, and non-volatile charcoal.

The process is carried out in : (a) pits or heaps (*meiler*), (b) closed ovens or retorts. The charring of wood in *meiler*, ordinary **charcoal burning**, is very old ; it is described by Theophrastos (315 B.C.). A rough central chimney is built and billets of wood stacked round it in a conical pile, the whole being covered in with turf (Fig. 273). A lighted faggot is dropped down the chimney, to kindle the wood, which burns *slowly*, just sufficient air being admitted through holes at the bottom. After some days the luminous flame from the chimney is replaced by a blue flame of carbon monoxide. All the air holes are now stopped up, and the charcoal allowed to cool.

In the modern process, based on Glauber's work, the wood is heated in externally fired ovens, or iron retorts, from which



FIG. 272.—THE LINKING OF CARBON ATOMS IN GRAPHITE.

air is excluded (Fig. 274). The volatile liquid products are collected, and the inflammable gas is used for heating the retorts. The liquid distillate consists of (*a*) a watery portion, the pyro-

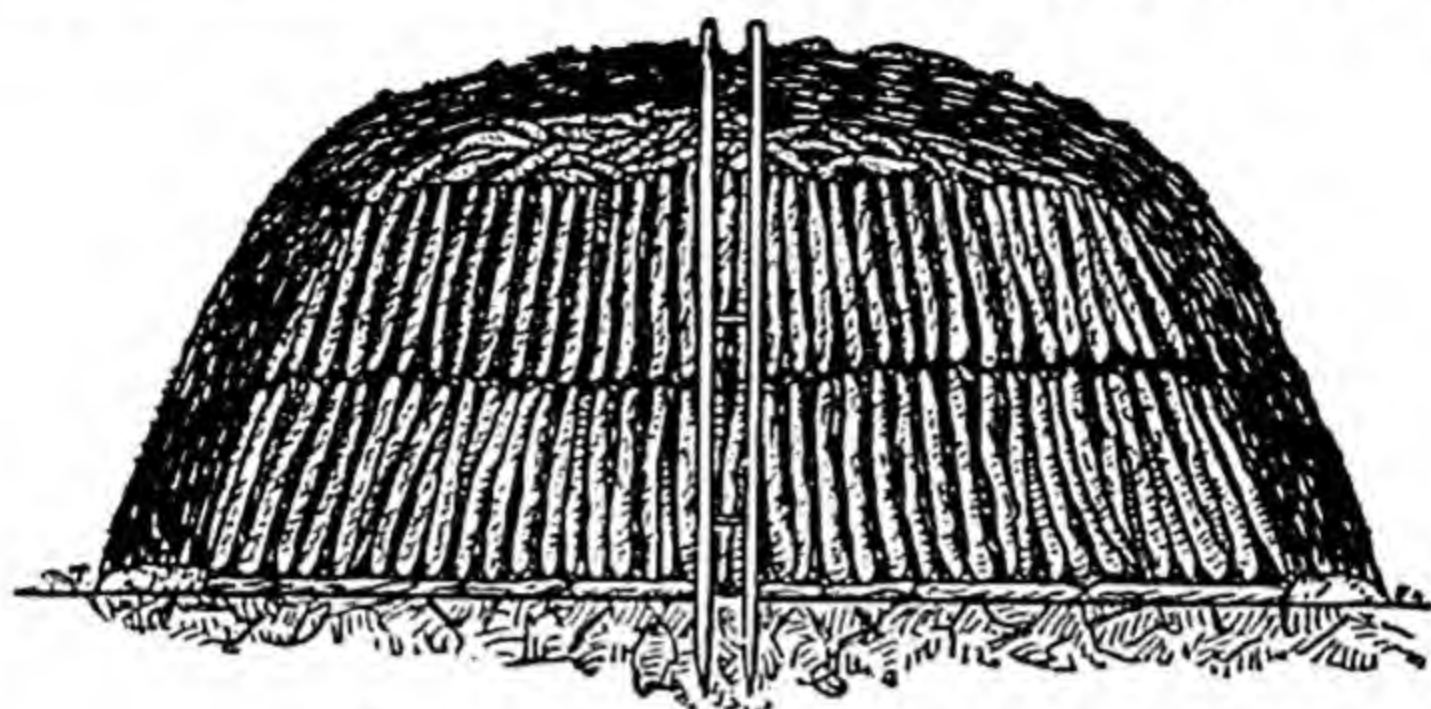


FIG. 273.—CHARCOAL MEILER.

ligneous acid, containing water, acetic acid, methyl alcohol, and acetone, which are extracted; (*b*) tar, which is valuable (*e.g.*, Stockholm tar, from pine wood).

Wood charcoal is a black, amorphous, friable material, retaining more or less the original shape of the wood, but diminished in volume. Although the specific gravity of air-free

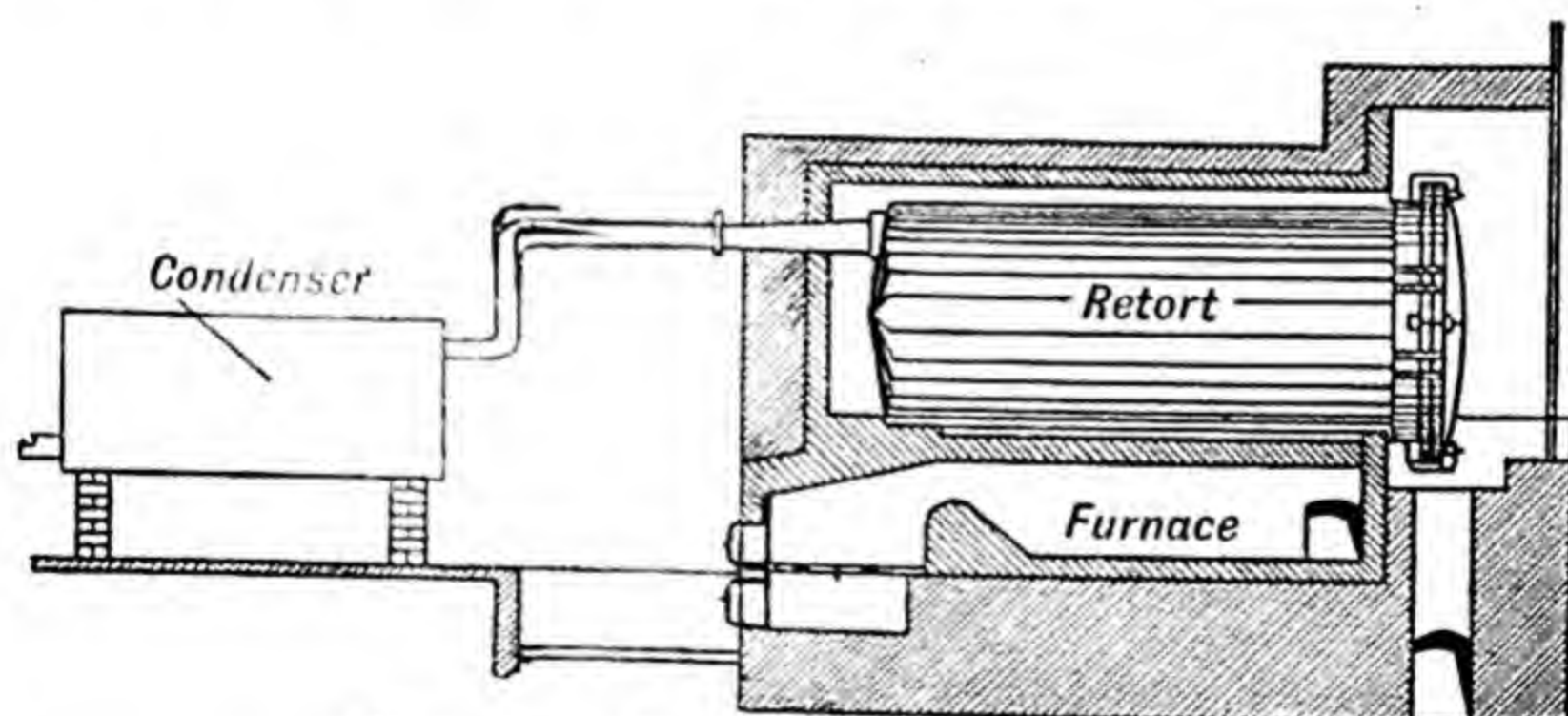


FIG. 274.—DISTILLATION OF WOOD.

charcoal is 1.4 to 1.9, the mass is very porous, and floats on water. If the air is removed by placing the charcoal in water in a bottle connected with an air pump, the charcoal gives out bubbles and slowly sinks. Charcoal is very permanent on exposure to air and moisture; charred oak stakes, planted in the bed of the



Thames by the Britons to resist the advance of Julius Caesar, were found still sound at heart.

In virtue of its great porosity, charcoal readily adsorbs gases, *i.e.*, condenses them on its surface. If a piece of recently ignited wood charcoal is passed into a tube of ammonia gas standing over mercury (Fig. 275), the gas is rapidly adsorbed; the charcoal takes up about ninety times its volume of ammonia gas.



FIG. 275.—ADSORPTION OF AMMONIA GAS BY CHARCOAL.

A very active form of charcoal is prepared by heating the shell of the coconut; 'active charcoal,' used in gas-masks, is obtained by heating charcoal, prepared at  $850^{\circ}$ - $900^{\circ}$ , in a stream of air, or in steam, when the material obstructing the pores is removed. It is also obtained by carbonising wood which has been treated with salts, such as zinc chloride or magnesium chloride, which are removed from the charcoal by washing with water or acids. It adsorbs very much larger volumes of gas than ordinary charcoal. Active charcoal is also used, as well as animal charcoal and blood charcoal, in decolorising sugar syrup, or for removing fusel oil (amyl alcohol) from crude spirit. This action may be illustrated by boiling some indigo solution with powdered animal charcoal and filtering. The liquid runs through colourless.

The decolorising charcoal is revived by boiling it with caustic soda solution and washing. Bone black is revived by heating to redness in closed retorts.

**Animal charcoal**, also known as *bone black*, is prepared by the distillation of bones in iron retorts. The volatile products are a watery liquid which contains ammonia, gases, and *bone oil* or *Dippel's oil*. The residue in the retort is a black mass containing about 10 per cent. of amorphous carbon disseminated through a very porous substrate, consisting of calcium phosphate, together with calcium carbonate, etc. If the phosphate and other salts are dissolved out by hydrochloric acid, the charcoal remains as *ivory black*.

**Lampblack** is a fine variety of soot, prepared as a pigment by burning natural gas, turpentine, tar, etc., in a limited supply of air, and collecting the soot by deposition. A very fine variety

for use as a pigment or as a filler in rubber tyres, is prepared from natural gas (*gas black*); another (*acetylene black*) from acetylene, at Shawinigan. Common lampblack is used in making printing ink and as a pigment. It contains some oily impurities which can be removed by heating in chlorine.

**Coal.**—Two varieties of amorphous carbon, coke and gas carbon, are derived from coal, and since some varieties of coal (anthracite) contain more than 90 per cent. of carbon, they will be considered here.

Coal is a carbonaceous mineral, which is the final result of a series of decompositions, which have occurred in the presence of a limited supply of air, undergone by vegetable matter of the remote past. High pressure, due to the weight of superimposed strata, was probably also necessary in these changes. A portion of the carbon, hydrogen, and oxygen was eliminated as carbon dioxide, water, and methane ( $\text{CH}_4$ ), and the residue became increasingly rich in carbon.

The first stage in the conversion of vegetable matter into coal is represented by **peat**, which consists of accumulations of vegetable matter, chiefly mosses and bog-plants, which have undergone partial change, and still preserve evidences of organic structure, although the deeper layers may be more compact and homogeneous. The next stage is represented by **lignite**, or **brown coal**, which is more compact than peat, and is lustrous, although impressions and remains of vegetable fragments, leaves, etc., are still distinct and numerous. Large beds of lignite occur, near the surface, in many parts of Germany, Hungary, and the Mississippi Valley, and are utilised as a cheap steam-raising fuel. **Jet** is a hard variety of cannel coal, used for ornaments.

The next stage of the process leads to the very important types of **bituminous coal**, *i.e.*, common coal. These are complex: distinct evidences of vegetable origin are still present, and the original plants are sometimes found fossilised. Bituminous coals burn with a bright smoky flame, and are further divided into **caking** and **non-caking** coals, according as they do or do not soften and fuse together on burning or coking. **Cannel coal** is a compact, non-lustrous variety, dull grey or black in colour, breaking with a conchoidal fracture, and yielding a large amount of gas and little coke. Splinters of cannel coal burn like candles when ignited, hence the name.

The latest stages in coal-formation consist chiefly of carbon, and are known as **anthracite**. Anthracite has a high ignition



point, usually a brilliant lustre, and a conchoidal fracture ; it does not burn with a flame, and gives very little smoke. It burns slowly and gives an intense heat on combustion. Anthracite occurs locally in many coal-fields, such as South Wales, Scotland, and Pennsylvania. Graphite may represent the ultimate stage of the decomposition, since it always contains a little hydrogen.

The following table shows the change in composition which occurs during the conversion of woody matter into coal, with the corresponding increase in calorific value (p. 412).

	Carbon.	Hydrogen.	Oxygen.	Calorific Value B.Th.U. per lb.
Cellulose - - -	44.5	6.2	49.3	7,500
Wood - - -	50.0	6.0	44.0	7,400
Peat - - -	60.0	5.9	34.1	9,900
Lignite - - -	67.0	5.2	27.8	11,700
Bituminous coal -	88.4	5.6	6.0	14,950
Welsh steam coal -	92.5	4.7	2.7	15,720
Anthracite - - -	94.1	3.4	2.5	15,720
Pure charcoal - -	100.0			14,544
Petroleum - - -	85.5	14.2	0.3	19,800
Coal gas - - -				19,220
Hydrogen - - -		100.0		62,100
Methylated spirit -	52.2	13.0	34.8	11,160

(The values for wood, peat, etc., refer to materials free from moisture : the actual materials contain water and the calorific values are smaller than those given. The values for pure charcoal, coal gas, hydrogen, methylated spirit, and petroleum are given for comparison.)

Powdered coal is converted into a hydrocarbon oil by heating it with hydrogen gas and coal oil under great pressure (the Bergius process).

**\*Smoke abatement.**—The conversion of raw coal into a smokeless domestic fuel by carbonisation at a temperature lower than that used in gas-making, leaving a residue which burns more readily than gas coke, is also the subject of much experiment at the present time. The use of gas is perhaps a more immediate solution of the problem of smoke. The economical utilisation of coal is, for Great Britain, a very important scientific problem, apart altogether from the prevention of smoke.

As at present burnt, coal is responsible for the production of vast quantities of soot and acid gases. It has been calculated that the deposit of soot in London amounts annually for each adult male inhabitant to his own weight. Another calculation states that, of the  $40\frac{1}{2}$  million tons of coal burnt for domestic purposes in Great Britain, the loss as smoke amounts to about  $2\frac{1}{2}$  million tons of potential fuel, but this is probably somewhat too large a proportion, although the cost for laundry work, painting and decorating, and the impairment of health caused by smoke are all very important.

Even when the smoke problem is solved, the problem of the emission of acid gases (sulphur dioxide) from the combustion of fuel remains to be dealt with. The amount of sulphur dioxide which would be emitted from the chimneys of one of the 'super power stations' would be enormous, and some means of removing this gas, say by washing the furnace gases, is necessary. The amount of sulphuric acid corresponding with the sulphur in the coal burnt annually in

London is from half a million to a million tons. The black particles of soot which settle out of the air may contain from 4 to 8 per cent. of free sulphuric acid, and they have a very destructive effect on vegetation and on stone work. The total deposit of solid matter from the atmosphere per square mile from October to March is 532 tons in Oldham, 286 tons in Liverpool, 263 tons in Manchester, 249 tons in London and 158 tons in York. It is estimated that 70 per cent. of London soot is due to domestic fires; in industrial towns the figure is probably about 30 per cent.

**\*Calorific value of fuels.**—The heat of combustion of a fuel such as coal is determined by burning a weighed amount of it inside a strong metal bomb (called a *bomb calorimeter*) (Fig. 276) containing compressed oxygen. The coal is contained in a little platinum spoon and is ignited by means of a small spiral of iron wire heated by an electric current and supported just over the spoon. (The known heat of combustion of

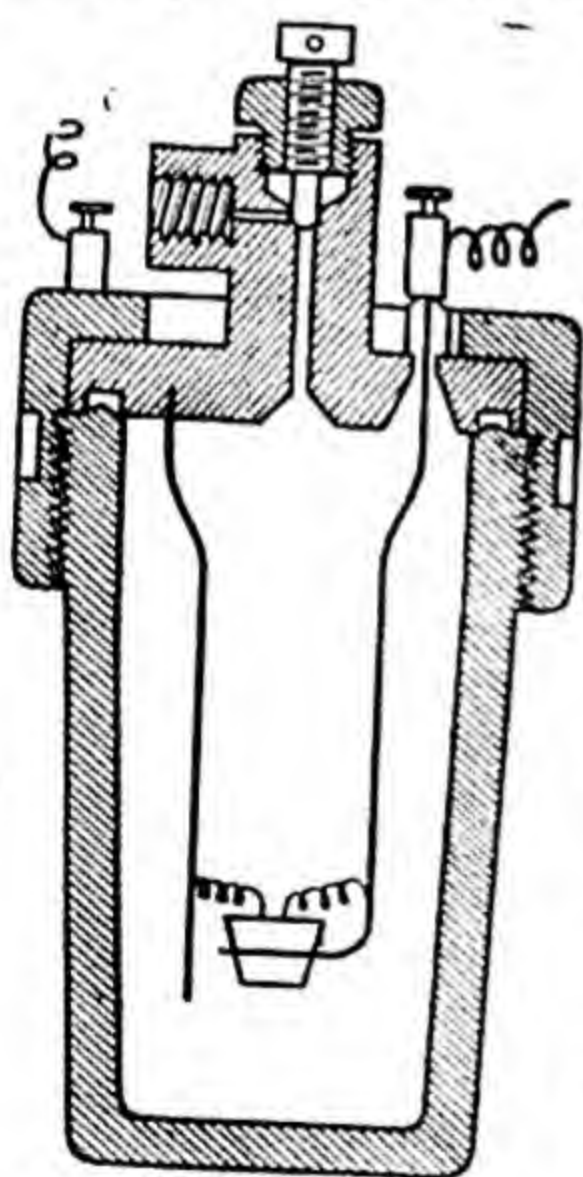


FIG. 276.—BOMB CALORIMETER.

contained in a little platinum spoon and is ignited by means of a small spiral of iron wire heated by an electric current and supported just over the spoon. (The known heat of combustion of



the iron is subtracted from the total heat evolved.) The bomb is immersed in water in a calorimeter and the rise in temperature of the water measured by a delicate thermometer. The calculation, which involves the 'water equivalent' of the apparatus, is made in the usual way. The result is usually called the **calorific value** of the fuel, and is given as the number of heat units produced by the combustion of unit weight of fuel. The calculation may take account of the condensation of the water produced in the combustion ('high value') or not ('low value'): in actual practice the water vapour will not usually be condensed and its latent heat will not be available. The calorific power of gas is determined by burning the gas in a special calorimeter of ingenious construction so that the calorific value is continuously and automatically registered by the apparatus itself.

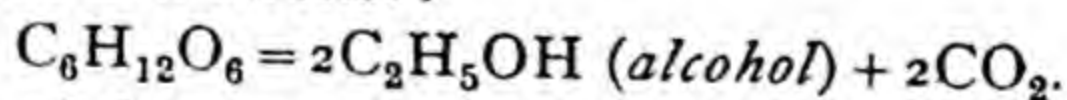
## CHAPTER XXIV

### THE OXIDES OF CARBON

**Carbon dioxide.**—There are two important oxides of carbon, both gaseous, viz. carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>. Both are of direct interest in everyday life.

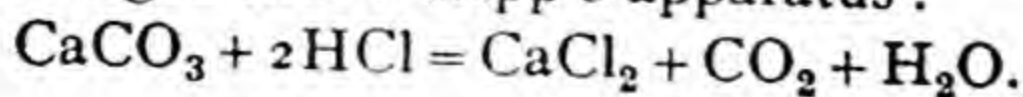
Carbon dioxide, called *gas sylvestre* by Van Helmont about 1630 (p. 78), was studied by Black (1754), who called it *fixed air*. Lavoisier in 1783 showed that it was an oxide of carbon, determined its composition by burning diamond and charcoal in oxygen, and called it *carbonic acid gas* because it was an acidic oxide, forming with basic oxides salts called *carbonates*. Many carbonates (chalk, marble, washing soda, white lead) are of importance, and mineral carbonates are common.

Carbon dioxide issues in abundance from the earth in certain localities, such as the Poison Valley (Java) and the Grotto del Cane (Naples). It occurs in many mineral waters, such as those of Selters and Vichy. By the combustion of carbonaceous fuels, large quantities of carbon dioxide pass into the atmosphere. The latter contains about 3 volumes of this gas in 10,000. Carbon dioxide is formed during respiration, as may be shown by blowing expired air through lime water, which becomes turbid owing to the precipitation of calcium carbonate. The fermentation of sugar, in the preparation of beer and wine, produces carbon dioxide and alcohol :



Other kinds of fermentation and the decay of organic matter also produce carbon dioxide, so that it is evolved from the soil.

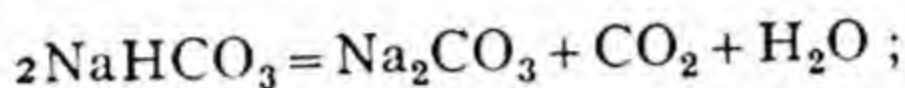
**Preparation of carbon dioxide.**—Carbon dioxide is *formed* by the direct combustion of carbon in oxygen, but is usually *prepared* by the action of acids on carbonates. Broken marble and dilute hydrochloric acid are the best materials to use, and they may be charged into a Kipp's apparatus :



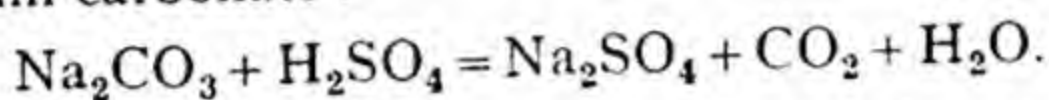


(Dilute sulphuric acid should not be used with marble, since the sparingly soluble calcium sulphate produced coats the marble and soon stops the action of the acid.) The gas is collected by downward displacement, since it is rather soluble in water and is  $1\frac{1}{2}$  times as heavy as air. It may be washed with water and dried by sulphuric acid or calcium chloride.

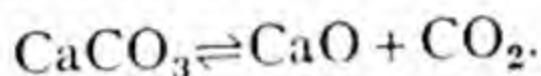
Pure carbon dioxide is obtained by heating pure sodium bicarbonate :



or by the action of dilute sulphuric acid boiled to expel air, on pure sodium carbonate :

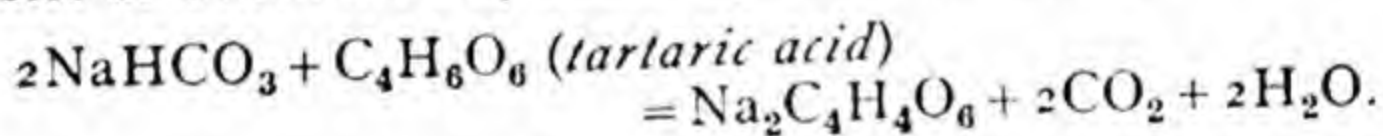


Carbon dioxide is evolved on heating carbonates ; all these except the normal carbonates of the alkali metals and barium carbonate, *e.g.*, chalk, limestone, marble, *magnesia alba*, etc., give off carbon dioxide at a red heat :



The gas is therefore produced in lime burning.

Baking powder contains sodium bicarbonate and tartaric acid, which do not react when dry. In presence of water, sodium tartrate is formed and carbon dioxide is evolved, the bubbles of which are expanded by heat on baking :



*Health salt* is a similar mixture. The fermentation produced by yeast in the baking of bread forms carbon dioxide, which gives the dough a spongy texture.

Sodium bicarbonate alone, and ammonium carbonate, which evolve bubbles of carbon dioxide on heating, are also used in baking.

**Properties of carbon dioxide.**—Carbon dioxide is a colourless heavy gas with a faint pungent smell and an acid taste. It extinguishes a burning taper, sulphur, phosphorus, etc. ; air containing  $2\frac{1}{2}$  per cent. by volume of carbon dioxide ceases to support the combustion of a taper, although  $18\frac{1}{2}$  per cent. of oxygen is still present. The gas is therefore used in extinguishing fires. If a little benzene is ignited in a porcelain dish, the flame is at once extinguished by the heavy carbon dioxide decanted upon it from a large jar.

Fire extinguishers (Fig. 277) consist of a strong metal vessel containing a solution of sodium carbonate, with a glass bottle of sulphuric acid inside. By means of a rod attached to a knob

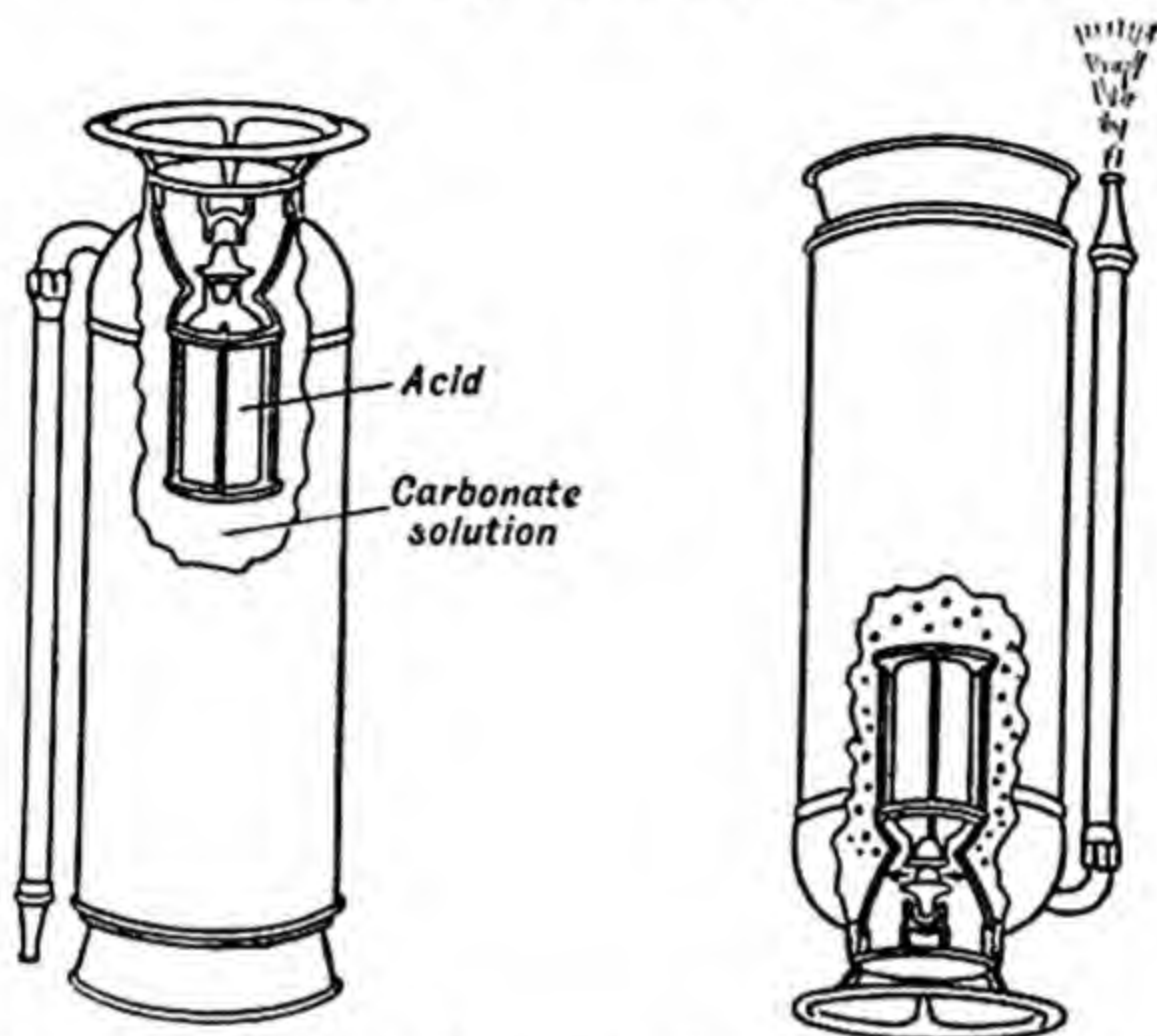


FIG. 277.—CARBON DIOXIDE FIRE EXTINGUISHER.

outside, the bottle may be broken, or the bottle may be inverted by tilting the extinguisher so as to pour the acid into the carbonate solution. The mixture of liquid and gas then issues forcibly from the nozzle.



FIG. 278.—PYRENE FIRE EXTINGUISHER.

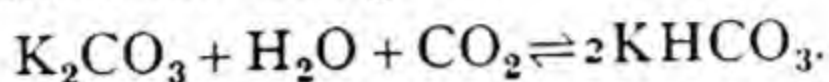
For extinguishing oil and petrol fires, *firefoam* is used. This is a froth of bubbles of carbon dioxide which floats on the burning oil, and is produced by mixing a solution of sodium carbonate containing liquorice (which causes foaming) with alum. Water alone sinks in burning oil and is almost useless.

Another type of extinguisher (*pyrene*) contains liquid carbon tetrachloride and a pump for spraying it on the fire (Fig. 278). The heavy vapour excludes air, and the fire goes out. In a strong wind it is not so effective.

Carbon dioxide is liquefied without great difficulty by compression: its critical temperature is  $+31^{\circ}$ . Carbon dioxide evolved in fermentation is collected for use in America, but in Europe the commercial gas is produced from marble and acid, or by burning coke. The gas so formed by combustion



must be purified by washing with water, absorbing the carbon dioxide from it in potassium carbonate solution, when potassium hydrogen carbonate (*bicarbonate*) is formed, and decomposing this by heating, with evolution of pure carbon dioxide, leaving potassium carbonate for use again :



The *liquid*, obtained by compression, is sold in large steel cylinders, from which the gas may be taken by standing the cylinder upright with the valve above. If the cylinder is laid

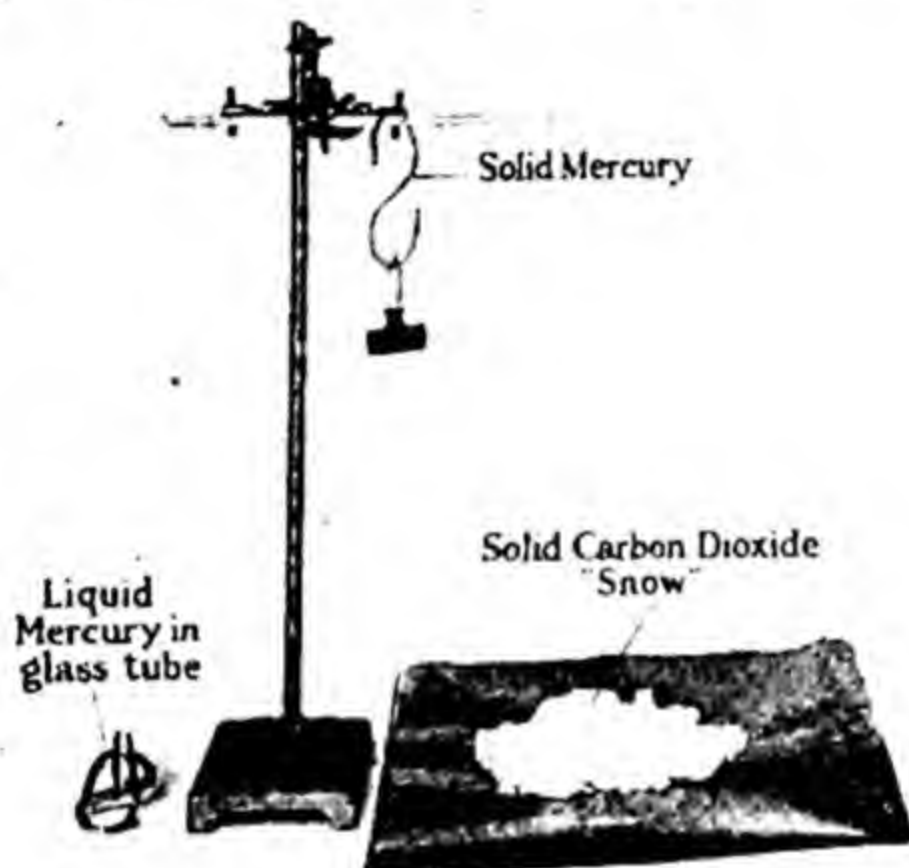


FIG. 279.—SOLID CARBON DIOXIDE AND FROZEN MERCURY.

on its side, and the valve opened, a jet of liquid carbon dioxide issues from it, which, owing to further cooling by rapid evaporation, at once freezes to a snow-like *solid* (Fig. 279), which may be collected by firmly tying a canvas bag to the jet. The solid is now made industrially and called *dry ice*, as it evaporates without residue, and is used for refrigeration. Mercury is rapidly frozen in a mixture of solid carbon dioxide and ether ( $-78^{\circ}\text{C.}$ ) (Fig. 279).

Carbon dioxide gas does not support respiration: animals die in it from suffocation, but it is not poisonous. The presence of the gas in cellars, wells, etc., is easily detected by the extinction of a lighted taper, which occurs with a proportion of carbon dioxide much smaller than any amount dangerous in respiration.

Burning magnesium ribbon continues to burn in a jar of

carbon dioxide, withdrawing the oxygen from the gas and setting free the carbon :  $2\text{Mg} + \text{CO}_2 = 2\text{MgO} + \text{C}$ .

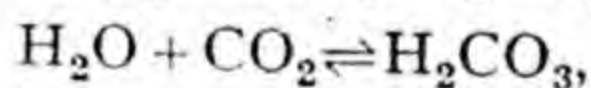
When the solid product of combustion is treated with dilute sulphuric acid the magnesia,  $\text{MgO}$ , dissolves and black specks of carbon are seen floating about in the liquid. In this way the presence of carbon in the gas may be demonstrated.

A characteristic reaction of carbon dioxide is the formation of a white precipitate of calcium or barium carbonate when the gas is passed into or is shaken with lime or baryta water. The calcium carbonate dissolves in excess of carbon dioxide to form a bicarbonate, but barium carbonate,  $\text{BaCO}_3$ , is insoluble (p. 298).

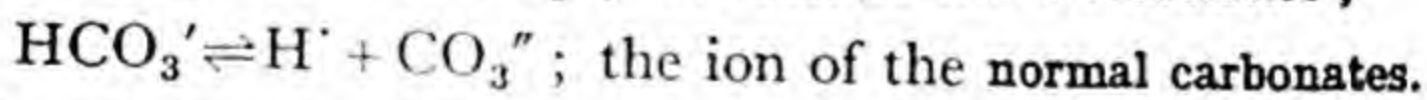
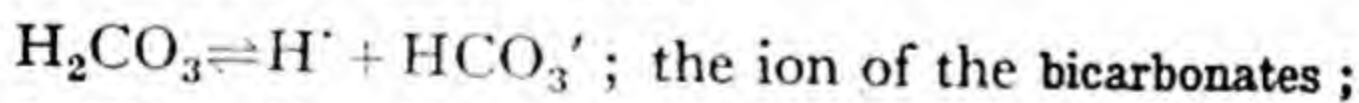
Water at room temperature dissolves about its own volume of carbon dioxide. Under pressure the amount dissolved increases. On lowering the pressure, the gas escapes with vigorous effervescence, although the liquid remains supersaturated, and evolves gas slowly for some time. If the liquid is stirred, or if porous solids such as sugar or bread-crumbs are thrown into it, brisk effervescence results. The whole of the carbon dioxide dissolved in water is expelled on boiling.

**Aerated waters** (*e.g.*, *soda water*) are charged with carbon dioxide gas under pressure; 'sparklets' are small iron bulbs containing liquid carbon dioxide.

**Carbonic acid.**—The aqueous solution of carbon dioxide has a faintly acid taste, and turns litmus a port wine red colour. If the amount of dissolved gas is increased by pressure, the litmus turns bright red. The liquid contains a very weak, dibasic, unstable carbonic acid, very probably  $\text{H}_2\text{CO}_3$  :



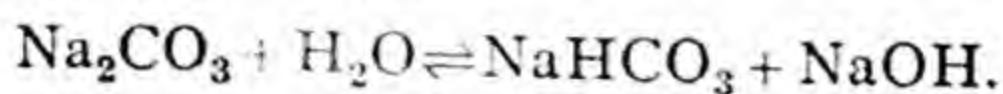
which forms two series of salts :



Sodium hydrogen carbonate, or sodium bicarbonate,  $\text{NaHCO}_3$ ; (normal) sodium carbonate,  $\text{Na}_2\text{CO}_3$ .

Calcium hydrogen carbonate, or calcium bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ ; (normal) calcium carbonate,  $\text{CaCO}_3$ .

In aqueous solution the normal carbonates react alkaline, owing to hydrolysis (p. 224) :





**The composition of carbon dioxide.**—The composition and formula of carbon dioxide are of great importance, because the amount of carbon in organic substances is determined by burning the substance, mixed with copper oxide, in a stream of oxygen and absorbing the carbon dioxide in weighed bulbs containing potash solution or soda lime. From the increase in weight of these bulbs, the amount of carbon dioxide evolved is found and thence, when the composition of carbon dioxide is known, the weight of carbon in the known weight of substance taken can be calculated. Since hydrogen is usually also present in organic substances, it burns to water, which is absorbed in weighed calcium chloride tubes placed *before* the apparatus for absorbing the carbon dioxide. Oxygen, if present, is estimated by difference. Nitrogen when present must be estimated separately.

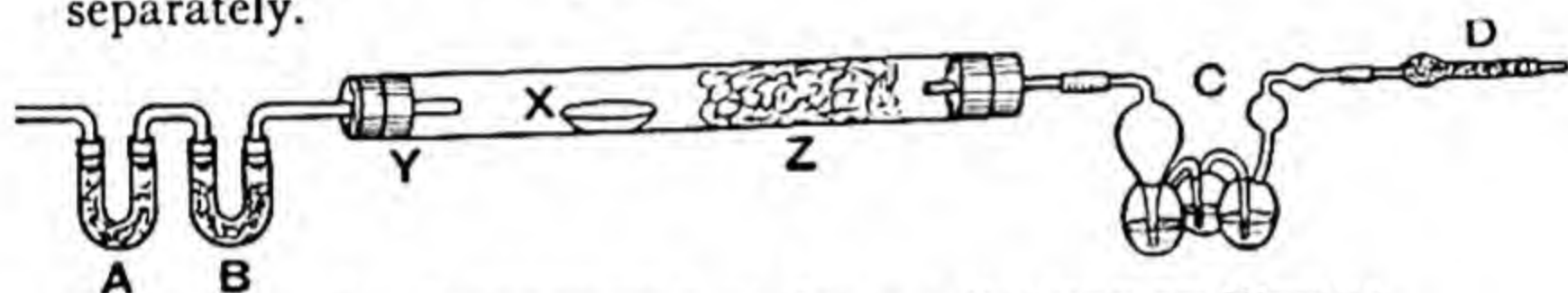
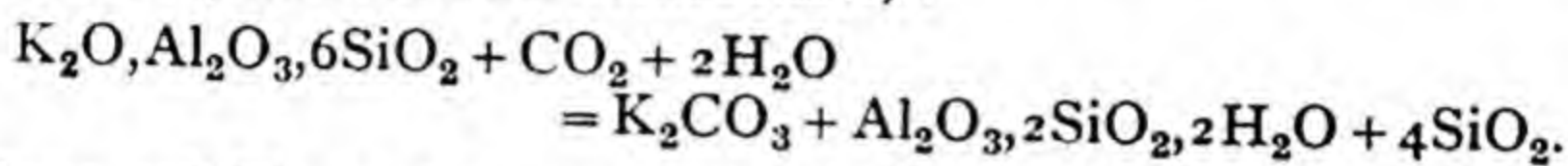


FIG. 280.—COMPOSITION OF CARBON DIOXIDE BY WEIGHT.

The composition of carbon dioxide *by weight* is found by burning a weighed amount of pure carbon (*e.g.*, diamond, or purified sugar charcoal) placed in a small porcelain boat, *X*, (Fig. 280) inside a hard glass tube containing a layer of copper oxide, *Z*, which is heated to redness in a furnace. The oxygen is first passed through purifying tubes containing broken sticks of caustic potash, *A*, *B*, which remove carbon dioxide and moisture. The carbon is heated, and burns. Some carbon monoxide ( $\text{CO}$ ) which is also formed is converted into carbon dioxide by the hot copper oxide, and the carbon dioxide is collected in the bulbs, *C*, containing potash solution which, with a calcium chloride tube, *D*, to prevent loss of moisture from the bulbs, are weighed. It is found that 12 parts of carbon combine with 32 parts of oxygen. By burning a piece of charcoal in oxygen in the apparatus shown in Fig. 234 it is found that *carbon dioxide contains its own volume of oxygen, i.e.*, the molecule contains a molecule of oxygen. The relative density is 22, therefore the molecular weight is 44. This contains one molecule of oxygen ( $\text{O}_2 = 32$ ) and, therefore,  $44 - 32 = 12$  parts, or one atom, of carbon. Hence the formula is  $\text{CO}_2$ .

**\*The carbon dioxide cycle.**—In early geological periods the atmosphere of the earth was probably very rich in carbon dioxide, whilst the primary rocks, such as felspar,  $K_2O, Al_2O_3, 6SiO_2$ , consisted almost entirely of bases (potash,  $K_2O$  and alumina,  $Al_2O_3$ ) in combination with silica,  $SiO_2$ . At high temperatures, silica displaces carbon dioxide from carbonates, forming silicates. As the temperature fell, the carbon dioxide and water in the atmosphere began to decompose the silicates, with the formation of free silica (quartz), aluminium silicates (clay), soluble alkali carbonates, and bicarbonates of alkaline earths (*e.g.*, potassium carbonate, and calcium bicarbonate) :



These soluble carbonates (*e.g.*,  $K_2CO_3$ ) were partly retained in the soil formed by this **weathering** or **pneumatolysis** of the primary rocks, and were partly washed away to the sea.

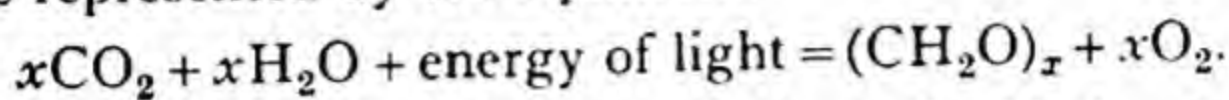
Meanwhile, the water of the sea had come into equilibrium with the atmospheric carbon dioxide, and dissolved a portion of it. The calcium and magnesium bicarbonates were utilised by marine organisms, which retained the normal carbonates, and set free half the carbon dioxide, which was again evolved to the atmosphere. When the organisms died, the calcium carbonate of their shells was deposited in the form of **chalk beds**, or **coral reefs** (a process which is still going on), producing **sedimentary rocks**. In this way carbon dioxide was largely removed from the atmosphere and stored up in the form of sedimentary rocks. It is estimated that, at present, about 30,000 times as much carbon dioxide is contained in rocks as exists free in the atmosphere.

The proportion of carbon dioxide in the atmosphere was thus considerably reduced, and further diminution occurred as a result of the *growth of green plants* under the influence of sunlight. The partial decomposition of the remains of these early plants led to the formation of **coal deposits**, in which the carbon is largely contained in the free state, or as hydrocarbons rich in carbon.

**The growth of plants.**—Green plants contain a green pigment known as **chlorophyll**, which may be extracted by boiling alcohol. This pigment occurs associated with protoplasm in the form of corpuscles known as **chloroplasts**, which are the active agents in the decomposition of atmospheric carbon dioxide by plants under the influence of sunlight.



Carbon dioxide is absorbed by all parts of the surface of the plant which contain chlorophyll, but mainly by the leaves, and it supplies the material from which the plant builds up its tissues. It is converted in the leaves, under the action of light, into **carbohydrates**  $(\text{CH}_2\text{O})_x$  (p. 403). The net result of this change may be represented by the equation :



The production of oxygen from carbon dioxide by the agency of living green plants under the influence of light is readily demonstrated by experiment. Watercress or mint is put into a flask filled with tap water and provided with an arrangement for collecting gas (Fig. 281). On exposure to bright sunlight, bubbles of gas rise from the leaves and collect in the test-tube. These consist largely of oxygen.



FIG. 281.—PRODUCTION OF OXYGEN FROM CARBON DIOXIDE BY GREEN PLANTS.

Priestley in 1771 showed that when sprigs of mint were placed in air which had been vitiated by respiration or by burning candles, the air was considerably improved. He later noticed that the 'air' given out in bubbles from plants immersed in water was much richer in oxygen than common air, and showed that this result was connected with the carbon dioxide dissolved in the water. He knew that light was necessary, but did not arrive at a clear understanding of the process.

Ingen-Houss in 1779 showed that light of sufficient intensity, carbon dioxide, and a *green* plant are necessary, and he also proved that the green part of a plant in the dark, and the roots both in light and darkness, vitiate the air in the same way as the breathing of animals. Ingen-Houss was not sure if this evolution of carbon dioxide also went on during exposure to light.

Theodore de Saussure in 1796 showed that when gaseous carbon dioxide is decomposed by green plants, the volume of oxygen set free is very nearly equal to the volume of carbon dioxide decomposed. This important result was confirmed by Boussingault in France, who suggested that a **sugar**,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is formed in the assimilation process, and disproved another

theory which had arisen, accepted by Saussure and Treviranus, that plants assimilate organic matter (*humus*) from the soil, rather than carbon dioxide from the air.

Plants require oxygen for their life processes, and evolve carbon dioxide. In the dark, when the photosynthesis is arrested, this respiration is the only process of gaseous exchange taking place: during the day much of this carbon dioxide may be decomposed by the chlorophyll.

In the leaves, the sugar first formed in photosynthesis is converted into granules of starch,  $(C_6H_{10}O_5)_x$ , when the cells containing chlorophyll contain an excess of sugar. These starch granules disappear in the dark and appear in some other part of the plant. It is supposed that solution of the starch by an enzyme called diastase (*q.v.*) occurs (p. 503).

Considerable quantities of water vapour are also given off from the leaves during photosynthesis.

**\*Plant fertilisers.**—Except in the cases of parasites (when the roots penetrate into the tissues of other plants and take up carbohydrates from them) or saprophytes (*e.g.*, fungi, which take up carbohydrates from dead organic matter), plants obtain all their food from inorganic materials.

Besides the *gases* mentioned above, plants require also *mineral matters*, which are absorbed in solution from the soil by the roots. These include combined nitrogen as nitrates; potassium, calcium, magnesium, and sodium salts; phosphates, chlorides, silica, and sulphur as sulphates. The normal soil always contains sufficient amounts of all these, except potassium salts, nitrates, and phosphates, which may have to be added in the form of manures, or fertilisers. Potassium salts are added in the form of potassium chloride or sulphate, or the crude potash minerals of Stassfurt. Combined nitrogen is supplied in the form of Chile nitre, ammonium sulphate, cyanamide  $CaCN_2$ , calcium nitrate, bone meal (containing phosphate), fish meal, flesh meal, blood, guano, and other nitrogenous animal products, and farmyard manure. It is in all cases converted before assimilation into nitrates by the activity of micro-organisms in the soil (p. 370). Phosphates are supplied as soluble superphosphate of lime, basic slag, bones, or other phosphates which can be dissolved by the carbonic acid evolved by decaying vegetable matter (*humus*) in the soil. Chalk, lime, and gypsum are applied to some soils. Small quantities of other elements (boron, manganese, iron) are said to be required for the sprouting of the seeds and the growth of plants,



and these are normally taken from the soil. The inorganic source of the food of normal plants was first clearly recognised by Liebig, who first laid down a rational theory of fertilisers.

One hundredweight of sodium nitrate or ammonium sulphate or  $1\frac{1}{2}$  hundredweights of cyanamide applied per acre increases the yield of potatoes by 1 ton, of wheat by  $4\frac{1}{2}$  bushels, of barley

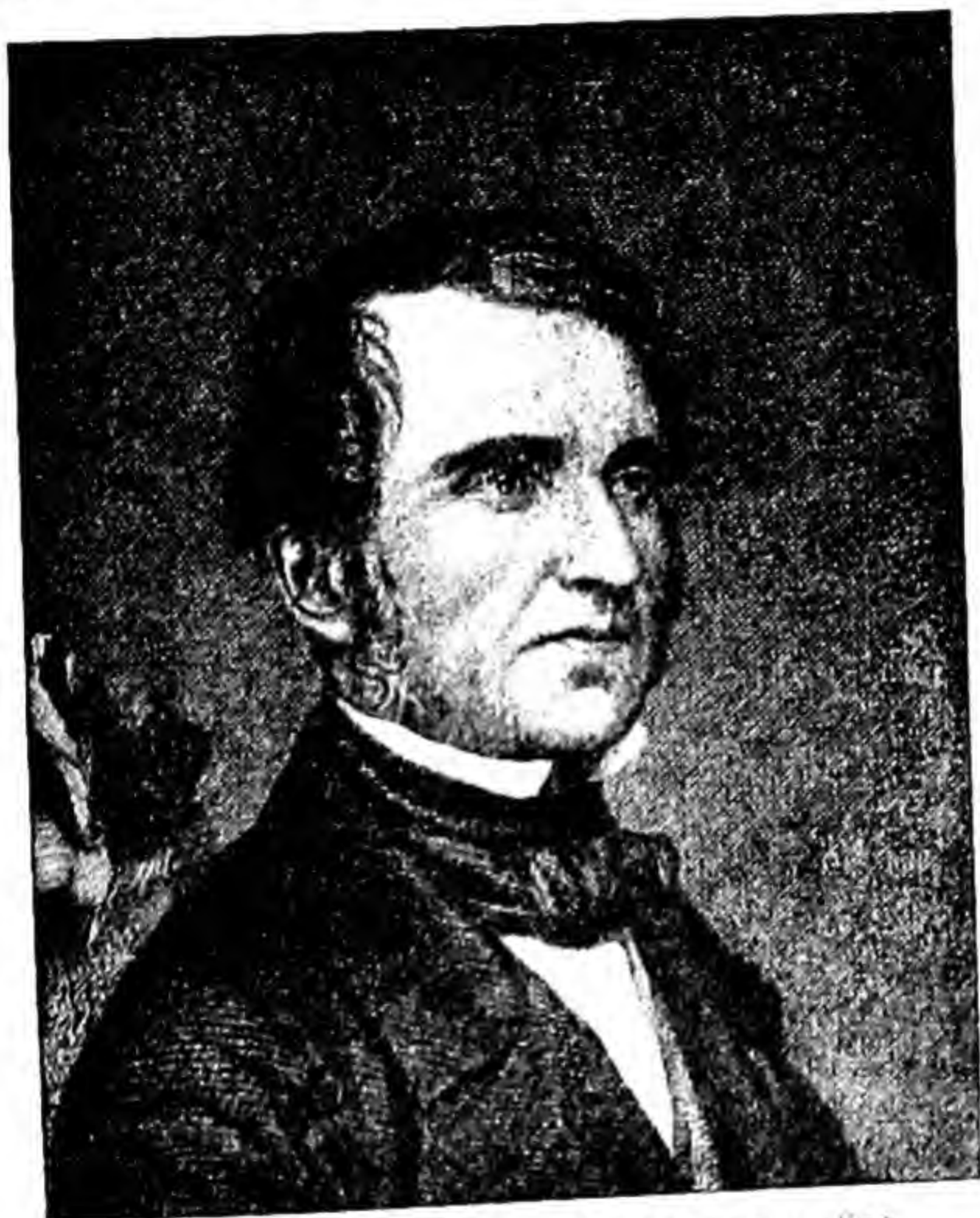


FIG. 282 — JUSTUS VON LIEBIG, 1803-1873

by  $6\frac{1}{2}$  bushels, and of oats by 7 bushels. One hundredweight of these fertilisers will therefore produce enough food to satisfy a man's requirements for a hundred or more days, or 1 lb. of combined nitrogen properly used in the soil will yield enough food to keep a man going for about five days.

By the activity of green plants, and of marine organisms (p. 420), therefore, the carbon dioxide content of the atmosphere tends to be reduced. We must now consider those processes

which tend to increase the atmospheric carbon dioxide. These are combustion and respiration.

**Respiration.**—Early experimenters, such as Mayow, Scheele, Priestley, and Lavoisier, were all aware of the great similarity between combustion and respiration. Lavoisier pointed out that the oxygen breathed into the lungs oxidises the carbonaceous materials of the blood, producing carbon dioxide, which is exhaled, and that *animal heat* is the result of this chemical process of oxidation (Fig. 283). The presence of carbon dioxide in



FIG. 283. — LAVOISIER'S EXPERIMENTS ON RESPIRATION.  
THE SUBJECT IS BREATHING AIR OR OXYGEN FROM A JAR STANDING IN A TROUGH THROUGH A TUBE FILLED IN A MASK. MADAME LAVOISIER IS SEATED AT THE DESK.

air from the lungs is easily demonstrated by blowing through a piece of glass tubing into lime water, when a white precipitate of calcium carbonate is produced.

The air passes into the lungs; these consist of hollow sacs, the surfaces of which are separated from the blood vessels by thin walls, through which the interchange of dissolved oxygen and carbon dioxide occurs. A certain amount of respiration takes place through the skin: this process is small in man, but is marked in some animals, such as frogs. In the case of fish, dissolved oxygen is absorbed by the gills.

Lavoisier thought that oxidation, with production of animal heat, occurred in the lungs but Mayow already knew that it



takes place in the tissues. The blood holds in suspension corpuscles containing a red colouring matter, **haemoglobin**, consisting of a coloured compound containing iron, called **haematin**, with the formula  $C_{34}H_{33}N_4FeO_5$ , the same in all animals, associated with a protein group called **globin**, which differs in different animals.

Haemoglobin absorbs one molecule of oxygen, producing a bright red substance, called **oxyhaemoglobin**, which exists in the blood of the arteries, passing from the lungs to the tissues. In the latter, the loosely-combined oxygen is absorbed, and oxidation processes occur. These are the source of animal heat and energy, and one of the products is carbon dioxide, which remains in solution as carbonic acid or bicarbonates. The de-oxygenated blood corpuscles have now a dark purple colour, and part of the blood containing them passes back to the heart by the veins, to be pumped to the lungs for re-oxidation.

The animal body may in some respects be compared with an engine, the material of which serves as its own fuel.

The expansion and contraction of the lungs, by which respiration occurs, are brought about by movements of the diaphragm and the ribs, both of which are co-ordinated by a nervous centre situated in the lower portion of the brain. This nervous centre works automatically; it is stimulated by the carbonic acid dissolved in the arterial blood passing through it, and the activity of the carbon dioxide appears to be due solely to its *acidity*, or the concentration of hydrogen ions in the blood. To maintain this acidity constant within very narrow limits is the function especially of the kidneys. The carbonic acid is expelled in the lungs in the form of carbon dioxide.

In consequence of the activities of plants and animals, the first absorbing carbon dioxide from the atmosphere, retaining the carbon and setting free the oxygen, and the latter absorbing oxygen and evolving carbon dioxide, a kind of *balance* is maintained between the proportions of oxygen and carbon dioxide in atmospheric air.

**Atmospheric carbon dioxide.**—Normal outdoor air contains about 3 volumes of carbon dioxide per 10,000. In crowded towns, and especially in rooms not sufficiently ventilated, the proportion of carbon dioxide may rise to 0.04-0.3 per cent. by volume. The continued breathing of air containing 0.2 per cent. of carbon dioxide is injurious (Angus Smith). The 'stiffness' of badly ventilated spaces is chiefly the effect of the water vapour exhaled by the lungs, which tends to saturate the stagnant air,

and impedes the evaporation of perspiration. One important function of ventilation is to keep the air in motion, so that the evaporation of moisture from the skin is not retarded.

The total amount of carbon dioxide in the atmosphere corresponds with about 600,000 million tons of carbon. The sources of atmospheric carbon dioxide are : respiration of animals and plants, combustion, fermentation, putrefaction, the soil (worms, decay, and gas of volcanic origin), mineral springs, volcanic activity, and lime-burning. Atmospheric carbon dioxide is diminished by : absorption by the sea, photosynthesis by green plants, and the weathering of rocks ( $1.62 \times 10^9$  tons of carbon dioxide per annum). On the whole, the proportion of carbon dioxide in the atmosphere appears to be slowly increasing, and slight changes of climate may be due partly to this cause.

### CARBON MONOXIDE.

**Carbon monoxide.**—Above a clear fire are seen flickering blue flames. Carbon is not volatile, and we should not have expected it to burn with a *flame* if carbon dioxide were produced directly. The flame is due, in fact, to a gaseous lower oxide of

carbon, carbon monoxide,  $\text{CO}$ , burning to carbon dioxide.

Carbon monoxide (sometimes called *carbonic oxide*) occurs in coal gas, in the fumes from burning charcoal and in the exhaust from motor engines. The noxious character of all these gases is due to the carbon monoxide, which is an exceedingly poisonous gas ; it is particularly dangerous because it has little smell and acts so rapidly that collapse renders the victim incapable of escape from its influence.

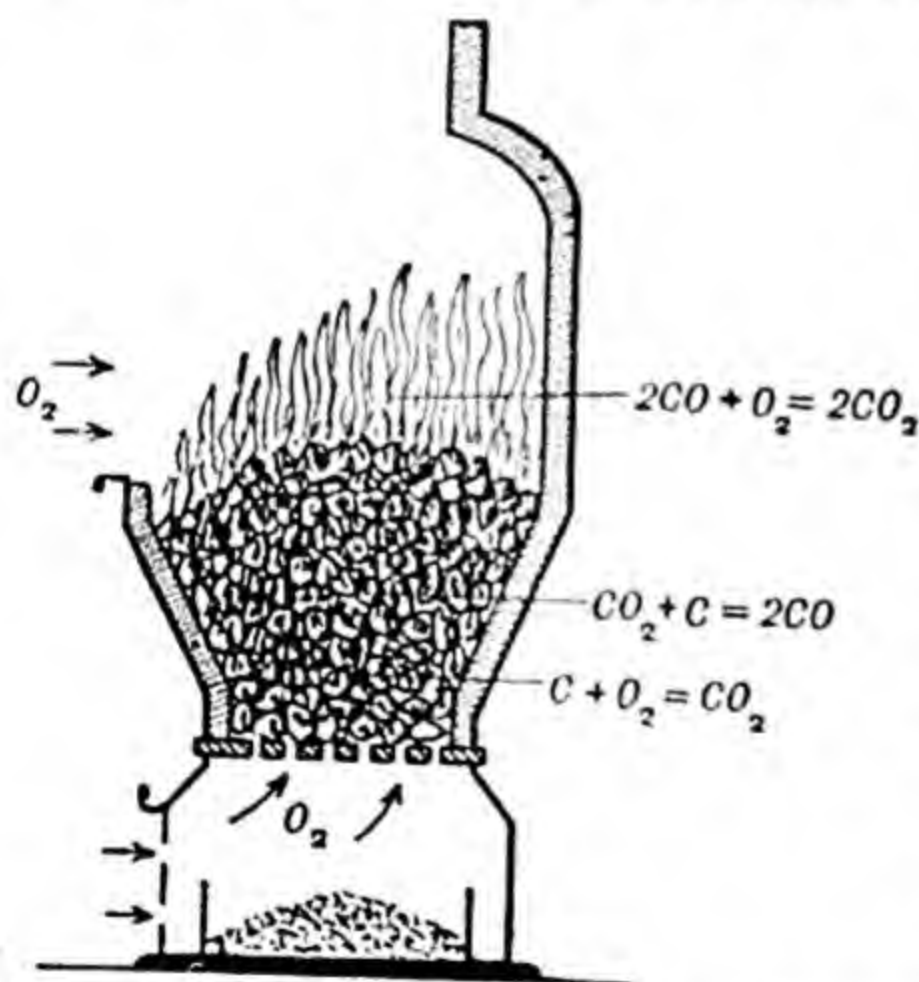
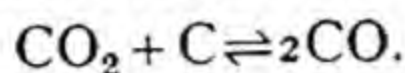


FIG. 284.—THE CHEMISTRY OF A COKE (OR CHARCOAL) FIRE.

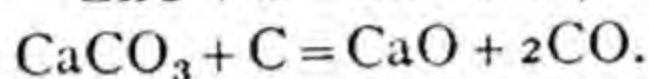
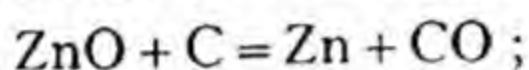
Carbon monoxide was obtained by Lassone in 1766 by heating charcoal with zinc oxide : its composition was determined by Cruickshank in 1800.



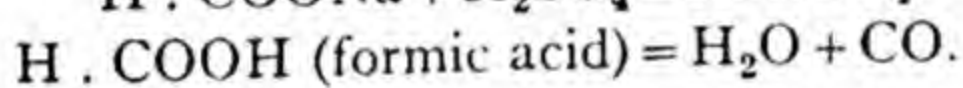
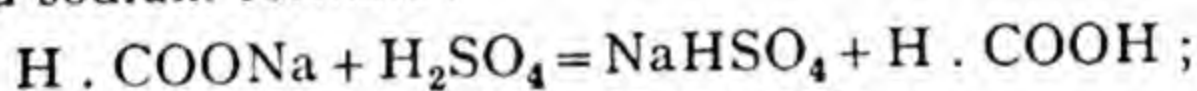
The formation of carbon monoxide in a fire is usually explained by the reduction of the carbon dioxide, produced in the lower part of the fire in presence of the free air, to monoxide in passing through the mass of incandescent carbon in the centre of the fire (Fig. 284). Carbon monoxide is, in fact, produced when a slow stream of carbon dioxide is passed through a strongly heated tube packed with charcoal :



Some chemists, however, consider that carbon monoxide is a primary product of the combustion of carbon. Carbon monoxide is also produced by heating the oxides of zinc, iron or manganese with charcoal, or charcoal with chalk (calcium carbonate) :

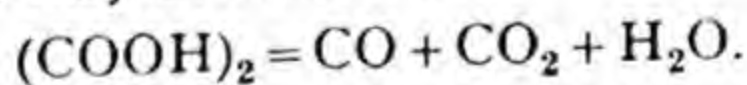


**Preparation of carbon monoxide.**—In the laboratory, carbon monoxide is most conveniently prepared by dropping concentrated sulphuric acid into formic acid or (more conveniently) on to solid sodium formate :

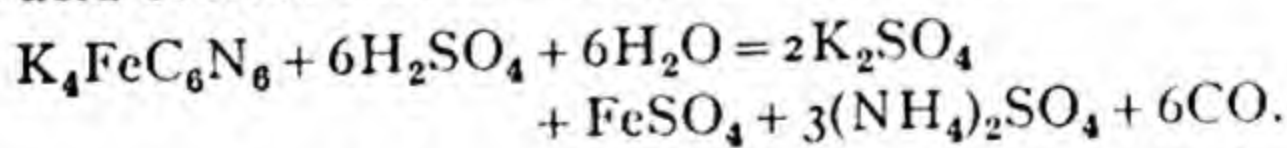


The sulphuric acid 'abstracts the elements of water' from the formic acid, leaving pure carbon monoxide, which is evolved as a gas and may be collected over water. It may be dried by sulphuric acid or calcium chloride and collected over mercury.

Crystals of oxalic acid, on warming with concentrated sulphuric acid, evolve a mixture of equal volumes of carbon monoxide and carbon dioxide. On passing the gas through a solution of caustic soda the carbon dioxide is removed and the carbon monoxide may be collected :



Potassium ferrocyanide on heating with concentrated sulphuric acid evolves carbon monoxide rather violently :



*Great care must be exercised in all experiments with carbon monoxide, as it is very poisonous.*

**Properties of carbon monoxide.**—Carbon monoxide is a colourless gas with a peculiar faint smell. It is very poisonous,

being absorbed by the haemoglobin of the blood to form a very stable bright red **carboxyhaemoglobin**, thus displacing oxygen from the blood and preventing it from combining with haemoglobin and so reaching the tissues. Many deaths have been caused by the carbon monoxide present in coal gas, in gas from coke and charcoal fires, and in the exhaust gas from motor engines.

The air in towns with much motor traffic may contain appreciable amounts of carbon monoxide. A recent analysis of the air in Paris streets showed the presence of 0.44 parts of carbon monoxide and 3.4 parts of carbon dioxide in 10,000 volumes of air. One volume of carbon monoxide in 800 volumes of air is fatal when breathed for half an hour, and even 0.1 vol. in 10,000 of air is said to produce unpleasant effects when breathed for some time. Giddiness and headache produced by riding in badly ventilated closed cars are generally due to penetration of exhaust gas from leaks, or gas escaping past worn pistons into the crankcase and thence into the car, or even by being blown by wind from the exhaust pipe through leaks in the floor. A properly ventilated closed car is quite free from danger.

Considerable attention is being paid in the United States to the concentration of carbon monoxide in tunnels carrying automobile traffic. It is assumed, on the basis of experiment, that 4 parts of carbon monoxide per 10,000 of air, by volume, is the maximum tolerable concentration. This produces no noticeable effect if breathed for one hour, but if endured for longer periods it may cause headache, nausea or weakness. A recording apparatus has been installed in the large new Hudson Tunnel in which a sample of the air (purified from moisture and other gases) is passed over a granular catalyst called *hopcalite* (consisting of 50 parts of manganese dioxide, 30 parts of cupric oxide, 15 parts of cobaltic oxide ( $\text{Co}_2\text{O}_3$ ) and 5 parts of silver oxide) which oxidises carbon monoxide, in presence of air, to carbon dioxide. Heat is evolved and the rise in temperature is recorded by thermocouples. Estimates of the carbon monoxide produced by various types of automobiles at a speed of 15 miles per hour gave 41 cu. ft. for small cars to 184 cu. ft. for large trucks, per hour.

Hopcalite may also be used in respirators, *e.g.*, in mines: in this case a preliminary drying of the air, say with calcium chloride in the respirator, is essential.

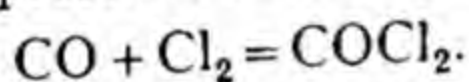
The ordinary charcoal respirator (or 'gas-mask'), mentioned



on p. 409, may be fitted with a cotton-wool filter to retain toxic smokes, but it is inactive towards carbon monoxide, so that it gives no protection, for example, against poisoning by coal gas, which contains carbon monoxide.

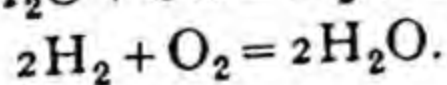
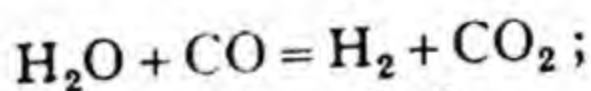
It is important to remember that dangerous amounts of carbon monoxide are formed by cooled gas flames, as in water heaters ('geysers'), and these should have adequate ventilation. Fatal accidents have resulted from the escape of gases from water heaters in bathrooms where the products of combustion were not properly removed.

The *after damp* (German *Dampf* = vapour) formed in coal mines after an explosion of *firedamp* (methane, see p. 437) owes its poisonous properties to carbon monoxide. Birds and mice are extremely sensitive to this gas, and miners in rescue parties generally take down canaries in cages to give warning of its presence. The compound of carbon monoxide and chlorine, carbonyl chloride, or *phosgene*,  $\text{COCl}_2$ , is also a very poisonous gas, and was largely used in chemical warfare. It is formed by direct combination in presence of sunlight or of charcoal :



Carbon monoxide is liquefied with much greater difficulty than carbon dioxide (cf. NO and  $\text{NO}_2$ ): it is sparingly soluble in water but is absorbed by a solution of cuprous chloride in hydrochloric acid or in ammonia. This may be used to separate it from other gases. Carbon monoxide forms compounds with some metals called *carbonyls*, e.g., nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , and iron carbonyls. These are usually volatile liquids.

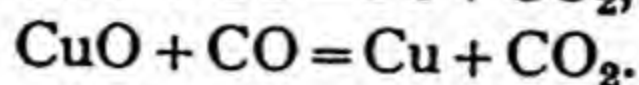
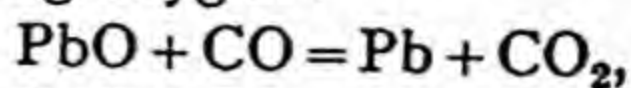
Carbon monoxide is *combustible*, burning in air or oxygen with a beautiful blue flame to form carbon dioxide. A mixture of carbon monoxide and oxygen is explosive. It is very curious that a *dry* mixture of the two gases is not explosive, and that a flame of dry carbon monoxide burning in ordinary air is extinguished when introduced into a jar of dry air. Dixon considered that the catalytic effect of traces of moisture corresponds with the reactions :



It has been shown that even a very dry mixture of carbon monoxide and oxygen can be exploded by a *very* powerful electric spark.

Carbon monoxide is a good *reducing agent*, and when passed

over heated metallic oxides it generally reduces them to the metals by withdrawing oxygen :



This property is made use of in many processes for the extraction of metals from the ores, the carbon of the fuel (*e.g.*, coke) being first converted into the monoxide by a limited supply of air, and the monoxide then reduces the heated oxide of the metal (*e.g.*, in iron smelting in the blast furnace). Gases containing carbon monoxide are used as fuels.

**Producer gas.**—This gas is principally a mixture of carbon monoxide and nitrogen obtained by passing air through a large mass of incandescent coke in an upright cylindrical furnace called a gas producer. The hot gas is then burnt where it is required by admitting a further quantity of air, when the monoxide burns to carbon dioxide.

**Water gas.**—This gas is a mixture of carbon monoxide, hydrogen, and some carbon dioxide, obtained by passing steam through incandescent coke. This reaction absorbs heat, so

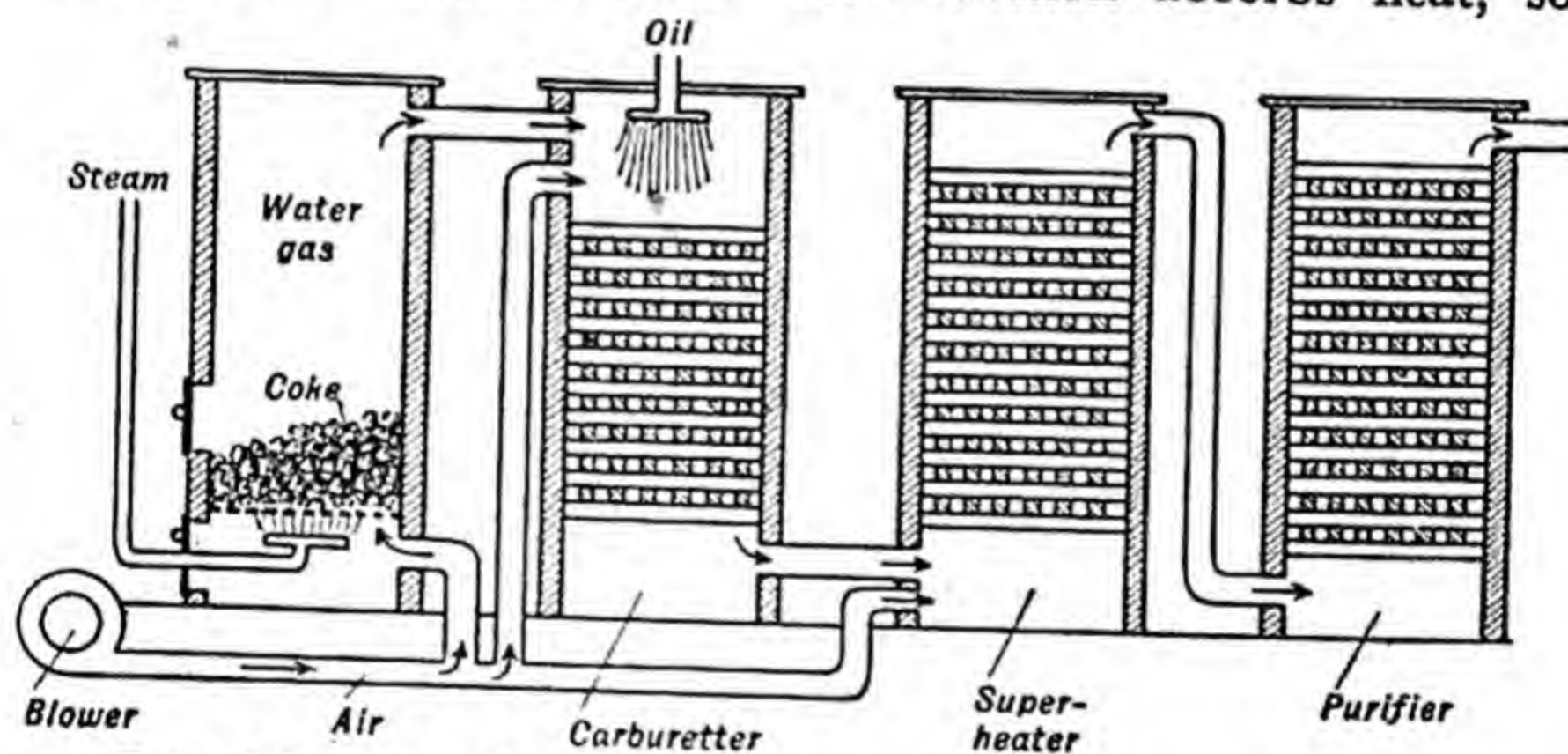


FIG. 286.—THE MANUFACTURE OF CARBURETTED WATER GAS.

that (unlike the formation of producer gas, which is an exothermic reaction) the formation of water gas must be frequently interrupted and the fuel brought to a high temperature again by blowing air through it. Two reactions between carbon and steam occur in the making of water gas :

- (1)  $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$  (*dull red heat*) ;
- (2)  $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$  (*bright red heat*).



Water gas also contains traces of sulphur compounds (chiefly sulphuretted hydrogen) from the coke, nitrogen (from air leakage), and a trace of methane. It burns with a blue, non-luminous flame, and is generally added to coal gas, since it has a good calorific power. To increase the illuminating power when burnt from common burners, the 'blue' water gas is 'carburetted' by passing it through hot brickwork over which oil is sprayed (Fig. 286). The oil vapour is decomposed ('cracked'), by heating, with the formation of hydrocarbons such as ethylene, which burn with a luminous flame, and these mix with the water gas. When incandescent mantles are used (as is now very generally the case) the actual illuminating power of the gas itself is of little importance, and modern coal gas, which is frequently mixed with water gas, is sold on its calorific, or heating, value (see p. 411).

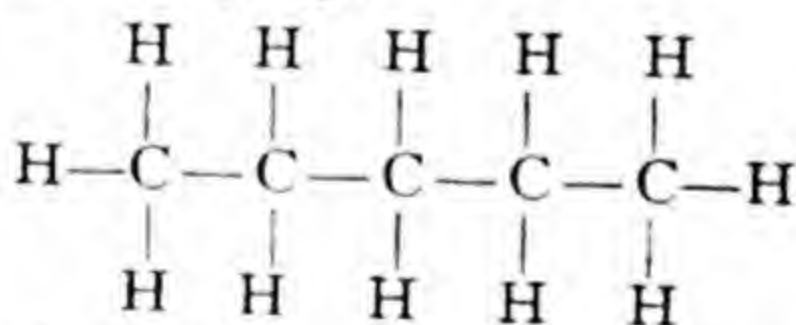
The Welsbach mantle is a tissue of 99 per cent. of thorium oxide, or *thoria*,  $\text{ThO}_2$ , and 1 per cent. of cerium dioxide, or *ceria*,  $\text{CeO}_2$ , both oxides being obtained from the *monazite sand* found in India (p. 43). Pure thoria gives out only a feeble light when strongly heated, but when mixed with 1 per cent. of ceria it glows brightly. The old type of mantle consisted of ramie-fibre cellulose, soaked in a solution of the thorium and cerium nitrates, to which some beryllium nitrate was added to confer toughness. The whole was then burnt off to form an oxide skeleton, which was impregnated with collodion to confer rigidity, the collodion being burnt off just before use. The modern soft mantles are composed of artificial silk impregnated with the nitrates and are not burnt off or collodionised before sale.

## CHAPTER XXV

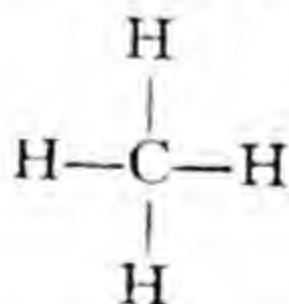
### HYDROCARBONS. FLAME

**\*Petroleum.**—Petroleum (mineral oil) consists of a mixture of various compounds of carbon and hydrogen, *i.e.*, of hydrocarbons. It is separated into various fractions by distillation, and the 'lighter' fractions (less dense, and of lower boiling points) contain hydrocarbons with smaller numbers of carbon atoms. The fraction between  $40^{\circ}$  and  $180^{\circ}$  is petrol, and consists chiefly of hydrocarbons  $C_6H_{14}$ ,  $C_7H_{16}$ ,  $C_8H_{18}$  and a few still higher homologues (*i.e.*, members of the series of hydrocarbons differing in composition by  $CH_2$ ).

The hydrocarbons present in American petroleum are mainly *saturated*, *i.e.*, they do not form addition compounds, because all the valencies of the carbon atoms are completely utilised in holding hydrogen atoms; they consist of open chains of carbon atoms, with the general formula  $C_nH_{2n+2}$ , beginning with the volatile liquid pentane  $C_5H_{12}$ :



The simplest member of this series is the gas methane,  $CH_4$ ,



which is not present in petroleum but is given off from petroleum wells. These hydrocarbons are also called **paraffins**, because they are chemically rather inert (Latin, *parum affinis* = little related).



The crude petroleum, a dark-coloured viscous oil, is distilled, the vapour passing into a fractionating column (*cf.* Fig. 323), and various fractions are taken off, which are afterwards purified.

The usual separation of the fractions is as follows :

Fraction.	Boiling point.
1. Petroleum ether or 'aviation spirit' - - - -	40°-70° C.
2. Naphtha (solvent) - - - -	80°-120° C.
3. Motor spirit - - - -	40°-190° C.
4. Burning oil (kerosene) - - - -	150°-250° C.
5. Fuel oil - - - -	250°-350° C.

The further fractions are distilled in a current of superheated steam and include :

1. Light lubricating oil.
2. Heavy lubricating oil.
3. Vaseline.
4. Paraffin wax (hydrocarbons from  $C_{18}H_{38}$  to  $C_{43}H_{88}$ ).

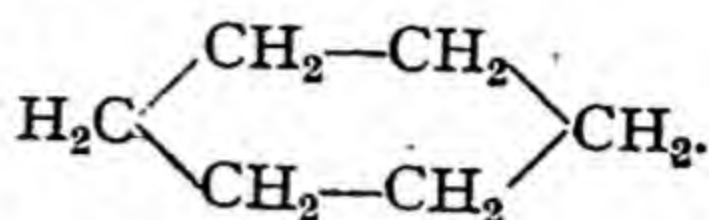
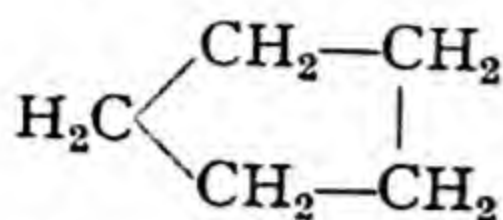
The residue in the retort is either bitumen or asphalt or (when the distillation is carried further) petroleum coke. (Vaseline and paraffin wax are *distilled* products, not residues.) Natural gas from oil wells is also cooled or passed over absorbent charcoal to remove very volatile hydrocarbons (chiefly pentane,  $C_5H_{12}$ , and hexane,  $C_6H_{14}$ ), called *casing-head gasoline*. This is blended with a less volatile material for motor fuel : it confers easy-starting properties.

**Paraffin wax** is also obtained by the distillation of *shale*, *brown coal*, or other material rich in organic matter, and occurs native as *ozokerite*, a mineral wax which is refined to produce *ceresin*. Great quantities of paraffin wax are used in making candles, for waterproofing paper and cloth, for coating metals to prevent rust, for electrical insulation, and other purposes. Scotland was formerly the principal producer, but America now produces 100,000 tons of paraffin wax a year, and Galicia, prior to 1914, exported annually 60,000 tons. Large quantities of paraffin wax are also produced from Rangoon petroleum.

The chief problem in **lubricant** manufacture is to produce a 'thin-thick' oil, one which is sufficiently mobile to enable a cold engine to be turned fairly easily, and is yet viscous enough at high temperatures, when the engine is working at speed, to maintain a film over the moving parts.

The hydrocarbons in Russian petroleum belong to a series called **naphthenes** ; they are saturated but differ from paraffins.

They have the general formula  $C_nH_{2n}$  and are **cyclic hydrocarbons**, as they have the carbon atoms arranged in closed rings. Such, for example, are **cyclopentane** and **cyclohexane** :

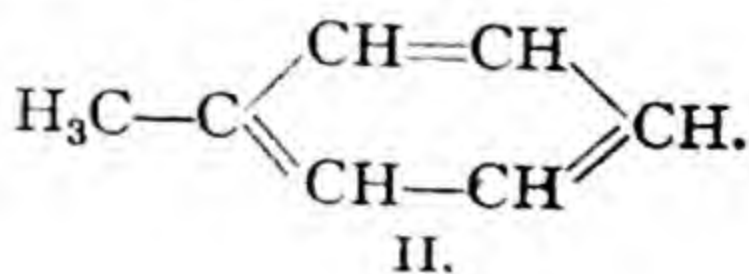
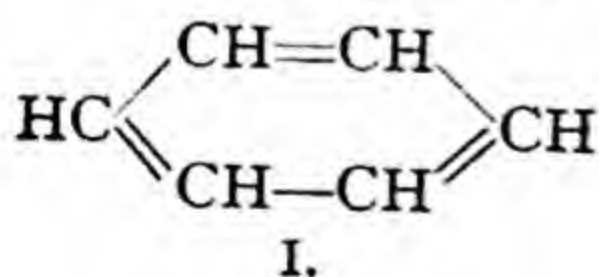


Considerable quantities of **petrol** (*motor spirit*; *gasoline*) are manufactured from heavier oils by the process of **cracking**. The oil is heated with exclusion of air, generally under pressure, when the heavier hydrocarbons decompose with the formation of lighter hydrocarbons, gas, and a heavy residue. This 'cracked spirit,' which usually contains unsaturated hydrocarbons, is very little liable to give rise to 'pinking,' or detonation, in motor engines. To prevent this, benzene may be added ('benzol mixture'), which burns more slowly than ordinary petrol, or else 'dopes,' such as tetraethyl lead ('ethyl'),  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , mixed with the petrol.

When tetraethyl lead is used, ethylene dibromide,  $\text{C}_2\text{H}_4\text{Br}_2$ , is added to convert the lead into the relatively volatile lead bromide, so that metallic lead does not deposit on the sparking plug points, and a chlorinated naphthalene called *halowax oil* is added as a valve-stem lubricant, the whole being coloured red for identification.

In cracking, part of the stock is up-graded but part is degraded into tar and coke. In the **hydrogenation** process all the stock can be up-graded into more valuable lower boiling distillates. The lubricating fraction is pumped under very high pressure with hydrogen gas through heated coils and then into heated reaction chambers containing the catalyst of molybdenum oxide on cubes of alumina. The molecules are rearranged and combined with hydrogen, while nitrogen, oxygen and sulphur impurities form hydrides, leaving the purified oil. The product is cooled and separated into gas and liquid, which is fractionated into gasoline, gas oils and a residue which is further treated for lubricant.

Some varieties of petroleum contain cyclic **aromatic hydrocarbons** such as **benzene** (I) and **toluene** (II) (p. 522) :





The petrol fraction of Borneo oil may contain 40 per cent. of these.

The heavy black residue in the retort left after the distillation of Californian or Mexican petroleum is composed of complex hydrocarbons and of organic compounds containing oxygen, nitrogen, and sulphur. It is called **asphalt**. A natural asphalt or **pitch** also occurs in some parts of the world, notably in the famous Trinidad Lake, which contains several million tons. Trinidad asphalt is solid and does not fuse in boiling water. It always contains sulphur. All kinds of asphalt are used for roads and roofing, and the Trinidad asphalt is used in making black enamel. A lower melting product is **bitumen**; it is also found native and was used in ancient Babylonia for caulking ships, and in building in place of mortar. Coal tar pitch is used in road-making and in making briquettes from coal dust.

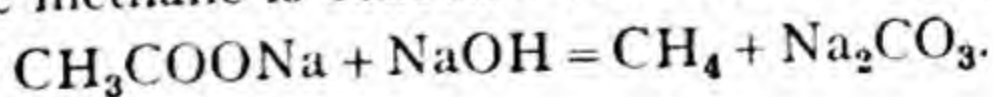
Three simple members of the hydrocarbon group will now be studied in greater detail.

**Methane.**—The first member of the paraffin series of hydrocarbons is methane,  $\text{CH}_4$ , which occurs mixed with carbon dioxide in *marsh gas*, formed by the bacterial decay of vegetable matter at the bottom of stagnant pools and liberated in bubbles when the mud is stirred. Methane is also contained in coal, and when the pressure is removed it escapes in the mines as *fire-damp*. This explodes when its mixture with air is kindled. The gas issuing from 'blowers' or fissures in coal may contain 80-98 per cent. of methane. *Natural gas* from petroleum wells contains over 90 per cent. of methane and is utilised for heating purposes.

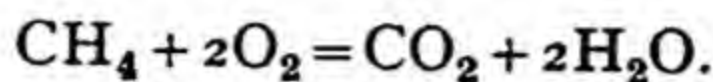
Methane is formed by direct synthesis when carbon is heated in hydrogen:  $\text{C} + 2\text{H}_2 = \text{CH}_4$ , but only in very small amounts. It is also produced when coal is heated to make coal gas. Methane is formed by the action of water on aluminium carbide:

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al}(\text{OH})_3 + 3\text{CH}_4.$$

Methane is prepared by heating anhydrous sodium acetate with three times its weight of soda-lime. The anhydrous sodium acetate is made by heating the crystalline salt on a clean sand bath until the water is driven off and the salt fuses, when it is cooled and powdered. The soda-lime is made by slaking quicklime with concentrated caustic soda solution and drying; it is less fusible than caustic soda and does not attack glass so easily. The methane is collected over water (Fig. 263):



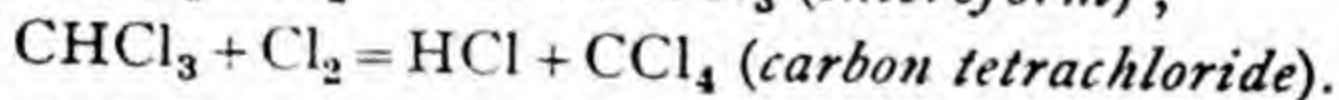
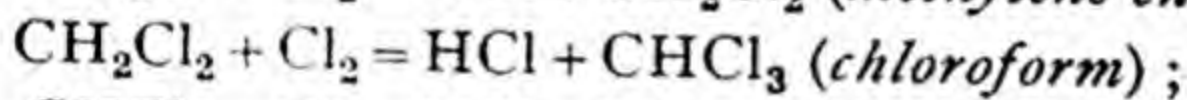
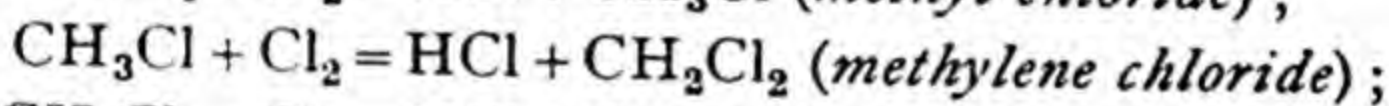
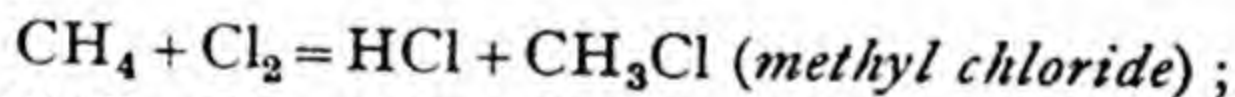
Methane is a colourless, odourless gas, liquefied only with difficulty. It is combustible, burning in air with a feebly luminous flame to carbon dioxide and steam :



It forms an explosive mixture with air or oxygen, the ignition of which causes explosions in mines. The poisonous *after-damp* formed in mine explosions contains carbon monoxide, formed by the incomplete combustion of the methane :



A mixture of methane and chlorine burns, when kindled, with a green-edged smoky flame :  $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$ . When a mixture of methane and chlorine is exposed to light the chlorine reacts by removing part or all of the hydrogen of the methane to form hydrogen chloride, and each atom of hydrogen removed is replaced by an atom of chlorine. Methane is a **saturated hydrocarbon**, *i.e.* all the valencies of the carbon are linked with hydrogen atoms, and reaction cannot occur by addition but only by substitution. Four products are formed :



\* **Methyl chloride** is a gas readily liquefied by pressure, and the liquid is used as a local anaesthetic and in some kinds of freezing machines to produce cold by evaporation. It is prepared from beet-sugar residues.

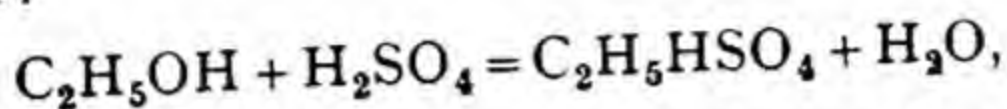
\* **Chloroform** is prepared by distilling alcohol or acetone with water and bleaching powder containing some free lime. It is a heavy volatile liquid used as an anaesthetic. Unless carefully purified it may contain the very poisonous phosgene (p. 429), to prevent the formation of which a little alcohol may be added.

\* **Iodoform**,  $\text{CHI}_3$ , the iodine analogue of chloroform, is formed by the action of iodine and aqueous alkali on alcohol or acetone. It is a yellow crystalline solid with a peculiar smell, and is used as an antiseptic.

\* **Carbon tetrachloride**, used in extinguishing fires (p. 416), is prepared by the action of chlorine on carbon disulphide (p. 453).



**Ethylene.**—The hydrocarbon ethylene,  $C_2H_4$ , is present in coal gas. It is prepared in the laboratory by heating a mixture of alcohol and concentrated sulphuric acid. The reaction, which involves the removal of the elements of water from the alcohol,  $C_2H_6O$ , occurs in two stages. Ethyl sulphuric acid is first formed :



and on heating in the presence of concentrated sulphuric acid this decomposes :

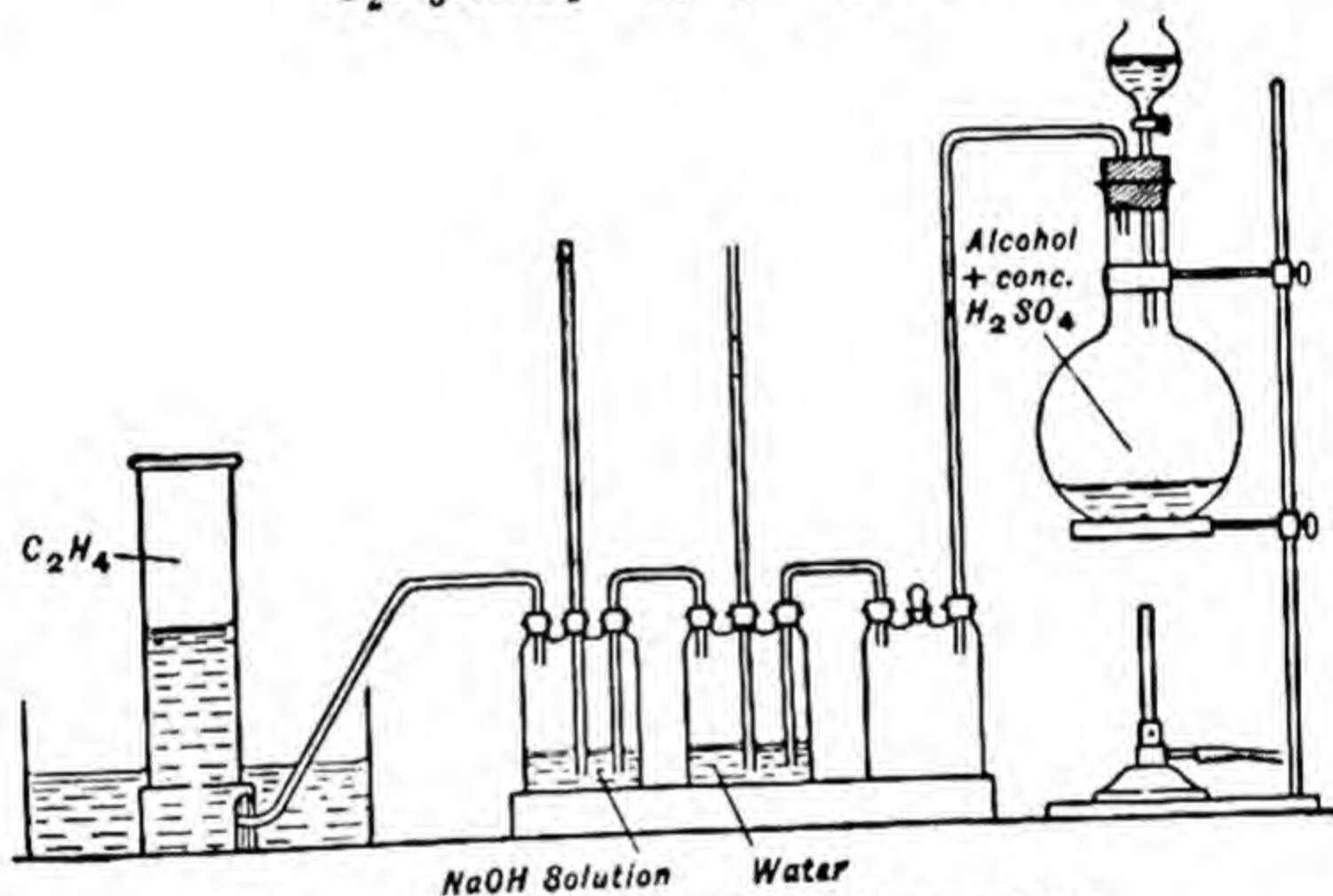
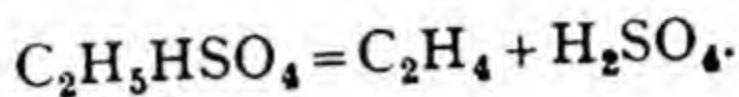
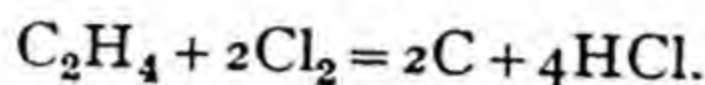


FIG. 289.—PREPARATION OF ETHYLENE.

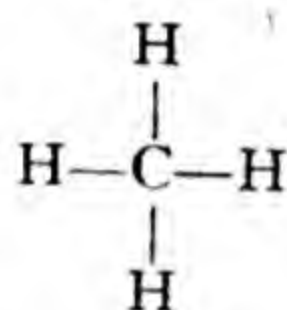
A mixture of 30 c.c. of alcohol and 80 c.c. of concentrated sulphuric acid is carefully heated in a 1 litre flask (since the mixture froths) and when the evolution of gas slackens a mixture of equal volumes of alcohol and concentrated sulphuric acid is run into the flask from a tap-funnel. The gas is passed through an empty Woulfe's bottle and then through water and caustic soda solution in two other Woulfe's bottles, to remove carbon dioxide and sulphur dioxide, and is collected over water (Fig. 289).

Ethylene is a colourless gas with a peculiar sweet smell; it is not poisonous and has anaesthetic properties. It is more soluble

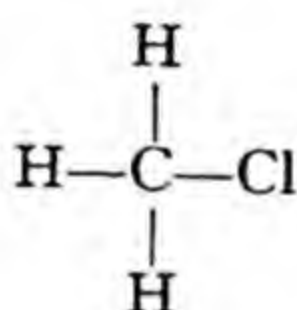
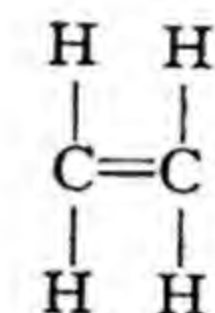
than methane in water. It burns in air with a luminous smoky flame, forming carbon dioxide, steam and a little free carbon. Its mixture with air or oxygen explodes when kindled. A mixture of ethylene and chlorine, when kindled, burns with a very smoky flame, clouds of carbon and fumes of hydrogen chloride being emitted from the jar :



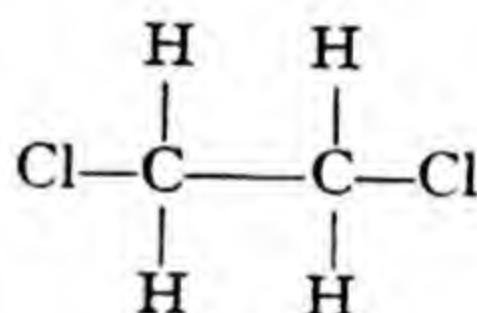
Ethylene differs from methane in being an **unsaturated hydrocarbon** ; the two atoms of carbon in its molecule are linked by a double bond, and for this reason the molecule will form compounds by direct addition, instead of by substitution as in the case of a saturated hydrocarbon. This is clear from the structural formulae :



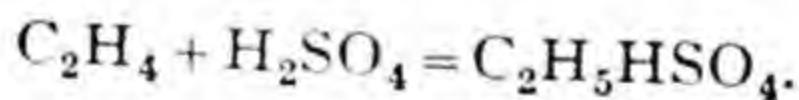
methane

methyl  
chloride

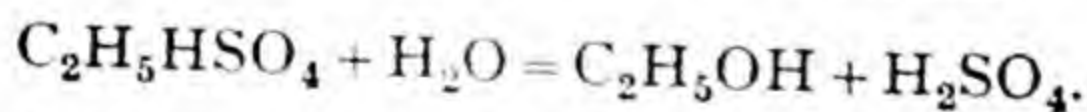
ethylene

ethylene  
dichloride

When a mixture of equal volumes of ethylene and chlorine is exposed to light, combination occurs and an oily liquid, **ethylene dichloride**, is formed :  $\text{C}_2\text{H}_4 + \text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$ . For this reason ethylene is sometimes called *olefiant* (oil-forming) *gas*. Ethylene is absorbed by concentrated sulphuric on shaking, and **ethyl sulphuric acid** is formed :



When this is boiled with water, alcohol is formed :



These reactions have been proposed for the technical production of alcohol from coke-oven gas, which is rich in ethylene.

**Acetylene.**—A familiar compound of carbon and hydrogen is the gas acetylene,  $\text{C}_2\text{H}_2$ , prepared for use in bicycle lamps by the action of water on calcium carbide. It was discovered by Edmund Davy in 1836, but was first carefully studied by Berthelot



in 1859. He showed that it is formed when ethylene or alcohol vapour is passed through a red-hot tube. Berthelot discovered the *direct synthesis* of acetylene from its elements, when an



FIG. 290.—BERTHELOT'S SYNTHESIS OF ACETYLENE.

electric arc burns between carbon poles in an atmosphere of hydrogen (Fig. 290):  $2C + H_2 \rightleftharpoons C_2H_2$ .

Acetylene is produced when a Bunsen burner, whether of the laboratory type or in gas stoves or gas-rings, 'strikes back,' *i.e.*, when the coal gas burns at the small jet, with a limited supply of air and in contact with the metal tube, which cools the flame. The peculiar smell noticed is usually said to be due to the presence of acetylene, the formation of which in the gas issuing from the burner is detected by holding over it a large globe wetted inside with an ammoniacal solution of cuprous chloride. The dark blue liquid rapidly becomes covered with a red film, owing to the precipitation of cuprous acetylide,  $Cu_2C_2$ , an explosive substance.

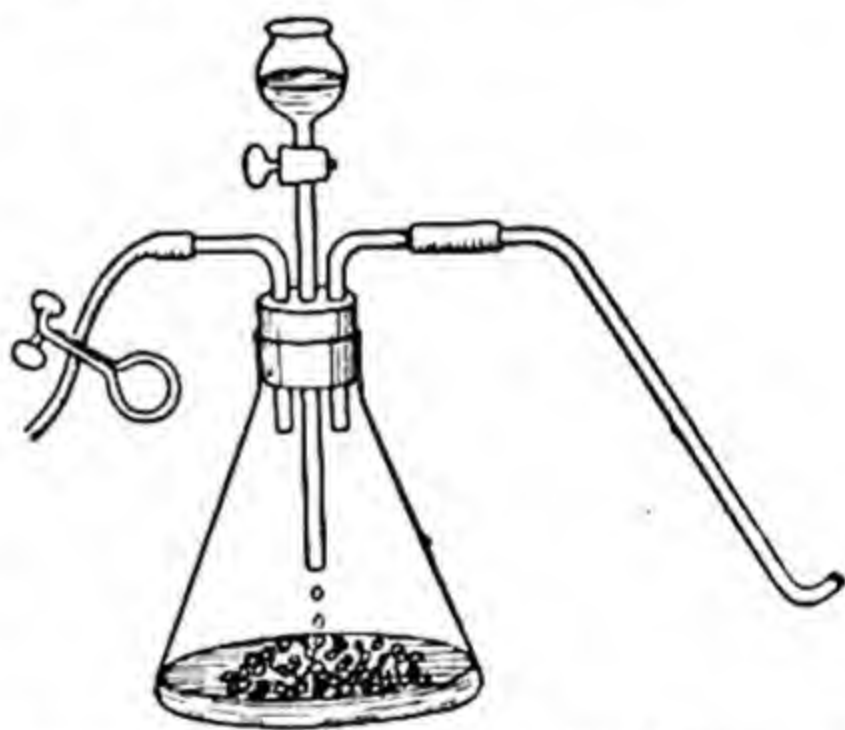


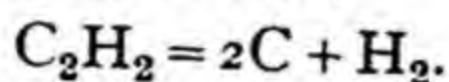
FIG. 291.—PREPARATION OF ACETYLENE FROM CALCIUM CARBIDE AND WATER.

Acetylene is best prepared by dropping water on calcium carbide (Fig. 291):  $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$ .

Various types of special generators for the gas are used when it is required for lighting purposes.

Acetylene is a colourless gas which is said to have an ethereal odour when pure but usually has an unpleasant smell. The pure gas is said to be non-poisonous and to have anaesthetic properties. It burns in air with a luminous, very smoky, flame,

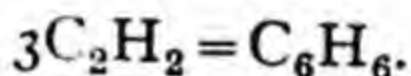
but when supplied to special burners it gives a very luminous white flame without smoke. A mixture of acetylene with air explodes when kindled, and the mixture with oxygen explodes with extreme violence, which may shatter even very strong glass vessels, so that it is unsafe to try the experiment with an ordinary eudiometer. The gas is explosive alone, since it is an unstable and endothermic compound and breaks down into its elements when exposed to pressure or shock :



When stored under pressure, the gas is therefore always first absorbed in liquid acetone soaked up in a porous material such as *kapok*, the seed hairs of a tree.

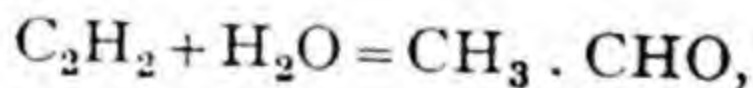
Acetylene is chiefly used as an illuminant and in the oxy-acetylene blowpipe for welding and cutting steel (p. 283) : it has been replaced to some extent for the latter by an oil gas (*blau gas*) rich in ethylene, or by coal gas.

When heated to dull redness, acetylene undergoes polymerisation (*i.e.* conversion of one compound into another of the same composition but higher molecular weight) and some benzene is formed :



In this reaction a straight-chain (*aliphatic*) hydrocarbon is converted into a ring (*aromatic*) hydrocarbon, and since acetylene is easily obtained by direct synthesis from the elements, its conversion into benzene amounts to a synthesis of the latter, and thence of its numerous derivatives.

Acetylene can be made to take up the elements of water, forming acetaldehyde :



and from the latter alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is formed by reduction, and acetic acid,  $\text{CH}_3\text{COOH}$ , by oxidation. These reactions have been used on the technical scale. By the regulated action of chlorine on acetylene in presence of other substances (*e.g.*, sulphur chloride) various compounds of carbon, hydrogen, and chlorine may be formed which are really chlorinated hydrocarbons. They are largely used as solvents for oils, fats, resins, etc., under such names as *westron* ( $\text{C}_2\text{H}_2\text{Cl}_4$ ) and *westrosol* ( $\text{C}_2\text{HCl}_3$ ). Westron is also used as a solvent for cellulose acetate dopes.

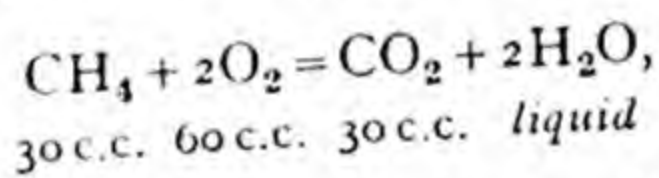
**The composition of hydrocarbon gases.**—The composition of methane, ethylene, or acetylene is determined by explosion with excess of oxygen in a eudiometer. In the cases of ethylene



and acetylene the explosion is very violent. Carbon dioxide and water are formed in each case. The water condenses on cooling and the carbon dioxide produced can be absorbed from the residual oxygen by means of a solution of caustic potash.

Let us suppose that 30 c.c. of methane are mixed with 66 c.c. of oxygen and the mixture exploded in a eudiometer. After cooling to the original temperature and adjusting the pressure, the residual volume is 36 c.c. This gas contains carbon dioxide and the residual oxygen. On treatment with caustic potash a residue of 6 c.c. of oxygen is left. The volume of carbon dioxide formed is therefore 30 c.c., or 1 vol. of methane gives 1 vol. of carbon dioxide, *i.e.*, 1 molecule of methane gives 1 molecule of carbon dioxide. The molecule of carbon dioxide contains 1 atom of carbon, hence the molecule of methane contains 1 atom of carbon.

The volume of oxygen used is  $66 - 6 = 60$  c.c. Of this, 30 c.c. will have been used to burn the carbon, hence 30 c.c. of oxygen were used to burn the hydrogen. Therefore the hydrogen present in 30 c.c. of methane requires 30 c.c. of oxygen, *i.e.*, the volume of hydrogen, if it existed as free  $H_2$ , would be 60 c.c. Thus one molecule of methane contains two molecules, or four atoms, of hydrogen. The formula is, therefore,  $CH_4$ :



Suppose 30 c.c. of ethylene are mixed with 95 c.c. of oxygen and exploded. The volume after explosion is 65 c.c. After absorption with caustic potash, 5 c.c. of oxygen remain. Thus 60 c.c. of carbon dioxide were formed, or 1 molecule of ethylene gives *two* molecules of carbon dioxide, *i.e.*, the ethylene molecule contains two atoms of carbon. The oxygen required for the combustion of the carbon will be equal in volume to the carbon dioxide, *i.e.*, 60 c.c. The total oxygen consumed is  $95 - 5 = 90$  c.c., hence 30 c.c. were used for the combustion of the hydrogen. Hence the 30 c.c. of ethylene contained hydrogen equivalent to 60 c.c. of free hydrogen, or 1 molecule of ethylene contains 2 molecules of hydrogen,  $2H_2$  or  $H_4$ . Hence the formula of ethylene is  $C_2H_4$ .

If 10 c.c. of acetylene are mixed with 30 c.c. of oxygen and exploded the residual gas occupies 25 c.c. After absorption

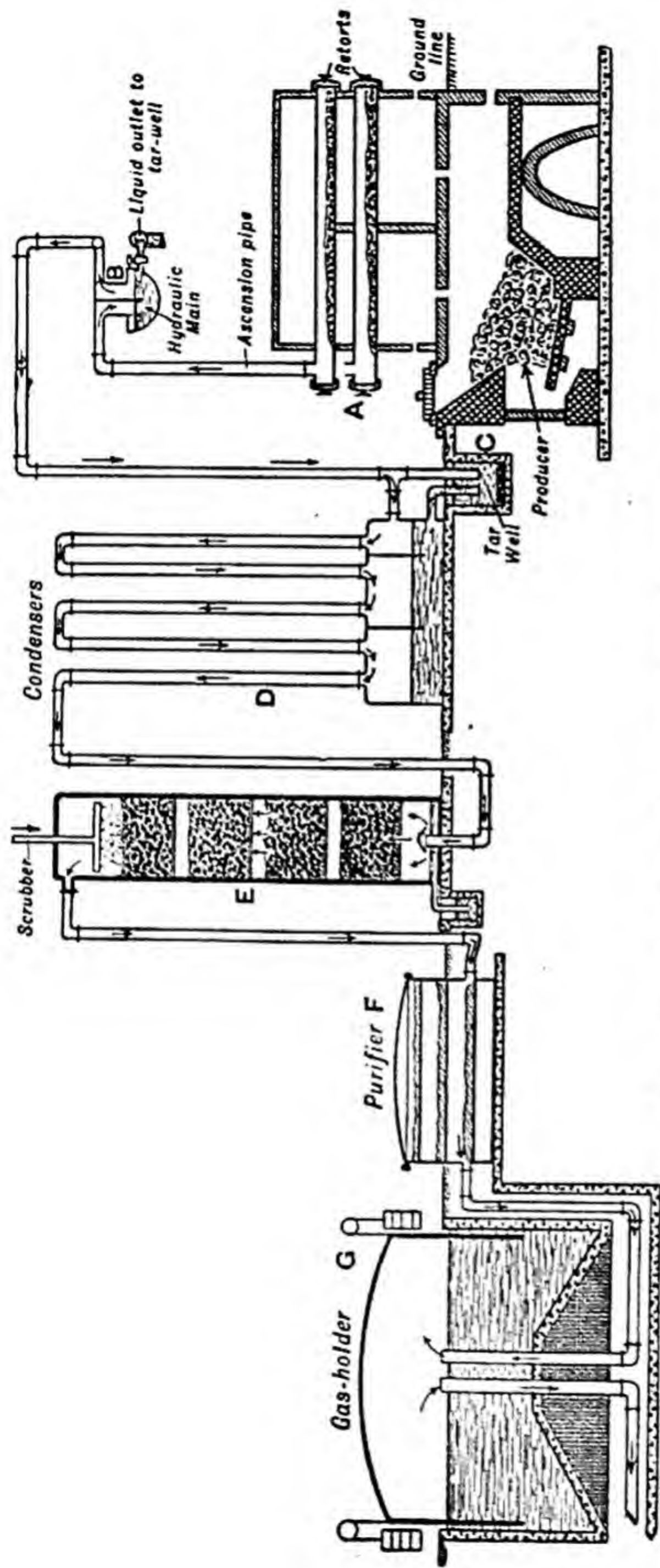


FIG. 292.—DIAGRAM OF A COAL GAS WORKS.

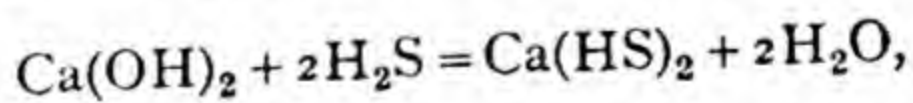
ON THE RIGHT TWO BANKS OF HORIZONTAL FIRE-CLAY RETORTS *A* ARE SHOWN IN SECTION. THEY ARE FITTED WITH DOORS AT EACH END TO FACILITATE REMOVAL OF THE COKE, AND ARE HEATED TO ABOUT  $700^{\circ}$  BY GAS MADE IN THE GAS-PRODUCER SHOWN BELOW. THE CRUDE GAS FROM THE RETORTS PASSES TO THE HYDRAULIC MAIN, SHOWN IN CROSS-SECTION AT *B*, IN WHICH IT IS COOLED TO ABOUT  $60^{\circ}$ , AND THE LIQUID WHICH SEPARATES PASSES TO THE TAR-WELL *C*. THE GAS THEN PASSES THROUGH THE AIR- OR WATER-COOLED PIPES OF THE CONDENSERS *D*, IN WHICH IT IS COOLED TO ATMOSPHERIC TEMPERATURE AND AS A RESULT MORE TAR AND AMMONIACAL LIQUOR ARE SEPARATED AND PASS INTO THE TAR-WELL. AFTER PASSING THROUGH EXHAUSTERS AND A TAR-SEPARATOR (NOT SHOWN IN THE FIGURE) THE GAS PASSES THROUGH WASHERS OR SCRUBBERS *E*, THE TYPE SHOWN BEING AN IRON TOWER CONTAINING COKE PACKED IN SECTIONS, OVER WHICH A STREAM OF WATER IS PASSED DOWNWARDS, THE GAS PASSING UPWARDS. THE WASHED GAS THEN PASSES THROUGH THE PURIFIERS *F*, CONTAINING SLAKED LIME OR HYDRATED FERRIC OXIDE, IN WHICH THE HYDROGEN SULPHIDE IS REMOVED. THE PURIFIED GAS THEN PASSES INTO THE GAS-HOLDER *G*, THE ONE SHOWN BEING OF THE WET TYPE AND DRAWN ON A MUCH SMALLER SCALE THAN THE REST OF THE APPARATUS.



with caustic potash the contraction is 20 c.c. and 5 c.c. of oxygen remain. Thus 2 molecules of carbon dioxide have been formed from 1 molecule of acetylene, or the latter contains *two* atoms of carbon. The oxygen consumed is  $30 - 5 = 25$  c.c., hence the hydrogen has required  $25 - 20 = 5$  c.c. of oxygen, corresponding with 10 c.c. of hydrogen. Thus the acetylene molecule contains its own volume of hydrogen, *i.e.*,  $H_2$ . Hence the formula of acetylene is  $C_2H_2$ .

**Coal gas.**—The distillation of coal, with the formation of gas, was first carried out by the Rev. John Clayton in 1688, the results being published in 1739. The use of coal gas as an illuminant was introduced by William Murdoch in 1792; in 1798 he installed a gas plant for lighting the factory of Boulton and Watt, at Soho, near Birmingham. Gas lighting was introduced into Manchester factories in 1805, the first public gas works being erected at Salford, and about the same time gas lighting was used on a very small scale in London. Houses were not lighted by gas until much later.

Coal gas is manufactured in **gas works** (Fig. 292) by heating bituminous coal in fireclay *retorts*, generally heated by producer gas. The gas evolved passes by way of vertical pipes from the retorts into a common *hydraulic main*, which serves as a water-seal, preventing gas passing back when the retort is opened. Ammoniacal liquor and tar separate in the hydraulic main, and crude gas passes on to the purifiers. Coke is left in the retort, and hard gas carbon is deposited on the red-hot part of the latter. The crude gas contains impurities, principally ammonia and hydrogen sulphide, which must be removed. It first passes to the *condensers* and then to a *scrubber*, where it is washed with water to remove the ammonia, which is valuable and is recovered from the ammoniacal liquor (p. 380). The hydrogen sulphide is then removed from the gas, in small works by passing over slaked lime in *purifiers*, which forms calcium hydrosulphide,



but in larger works by passing it over hydrated ferric oxide (p. 344).

The purified coal gas now passes to the *gas-holder*, a counter-poised iron bell sealed below by water, from which it is distributed for use.



The purified coal gas now passes to the *gas-holder*, of which there are two types. One (shown in Fig. 292) consists of a large inverted iron bell in a tank of water. The bell usually consists of sections sliding telescopically into each other, and guided by a steel outer framework, or else by inclined rails passing round the sections like a screw. The gas is now often dehydrated before it enters the holder by scrubbing with concentrated calcium chloride solution, and to prevent subsequent rewetting of the gas, the water in the holder is covered with a film of suitable oil.

The other type of holder is the 'waterless' type. This consists of a large vertical circular or polygonal tower of fixed dimensions, inside which a horizontal piston rises and falls, the gas being admitted and taken out below the piston. The upper side of the piston is open to the atmosphere in the tower. In order to seal the piston gas-tight around its edge, this is fitted with a flexible packing-ring of some suitable fabric, and tar is kept supplied by a pump round the edge of the piston. This type of holder has the advantage that the pressure, which can be adjusted by weighting the piston, is practically constant whatever the degree of inflation, whilst in a water-sealed holder the pressure increases with the lift of the bell.

In recent years gas undertakings have been purchasing coal gas from the coking industry, which has a surplus of gas when efficient 'recovery' or 'regenerative' coke ovens (p. 446) are used. This gas can be conveyed under pressure in pipes, and its long-distance distribution has been highly developed in Germany, where gas from pit-head coke ovens in the Ruhr district is fed to a large area in high-pressure mains. In the United States considerable use is made of coke oven gas for town supply, and the supplies of natural gas (principally methane, p. 435) from petroleum districts are also distributed for use. In most cases, coal gas is mixed with water gas, either made separately in gas producers (p. 430), or introduced into the gas by passing steam over the red-hot coke formed in a vertical retort.

The vertical retort is a rectangular or elliptical chamber of silica bricks (p. 472), heated outside by producer gas firing. The carbonisation process is continuous; fresh coal added to the top of the retort slowly travels down through it and undergoes carbonisation, and the coke is withdrawn continuously by an extractor from the bottom of the retort. Steam is admitted at the base of the retort, taking heat from the red-hot coke, reducing its temperature to about  $300^{\circ}$ , and forming water gas, which mixes with the coal gas passing out from the top of the retort.



At first, coal gas was nearly all used for domestic, industrial and street illumination by burning in open flame burners, when its illuminating power was the important factor. When the incandescent mantle was introduced, the heating value of the gas became most important (p. 284). This was also necessary when the use of gas for heating and cooking was extensively adopted. Nowadays coal gas is also largely used in industry for gas-heated furnaces, kilns, etc., and for power purposes.

The by-products of gas manufacture are also important, especially those from the tar (p. 523), but the by-product ammonia is not so valuable as it was, since very large quantities of ammonia are now made by the synthetic process (p. 378).

The average composition of unmixed coal gas, in percentages by volume, is as follows :

Hydrogen	-	-	-	-	43-55	} 'Diluents,' non-illuminating, but heat-producing.
Methane	-	-	-	-	25-35	
Carbon monoxide	-	-	-	-	4-11	
Olefins, acetylene and benzene	-	-	-	-	2.5-5	} Illuminants.
Nitrogen (from air leakage)	-	-	-	-	2-12	
Carbon dioxide	-	-	-	-	0-3	} Impurities.
Oxygen	-	-	-	-	0-1.5	

(The name 'olefin' is used for hydrocarbons of the formula  $C_nH_{2n}$ , like  $C_2H_4$ , ethylene or 'olefiant gas'.)

The hydrogen in coal gas is derived from the thermal decomposition of gaseous hydrocarbons in contact with the hot walls of the retort. The carbon formed is deposited as **gas carbon**, which is a very pure form of amorphous carbon, a good conductor of electricity, and used for the pencils of arc lamps or in electric batteries.

The luminosity of unmixed coal gas flames is due entirely to the 5 per cent. of olefin hydrocarbons, acetylene (0.06-0.07 per cent.), and benzene vapour.

The effect of such hydrocarbons on the luminosity of flames may be illustrated by fitting a small brass jet to each arm of a Y-tube, in one arm of which is a piece of cotton-wool soaked in benzene (Fig. 293), attaching the tube to a hydrogen apparatus,

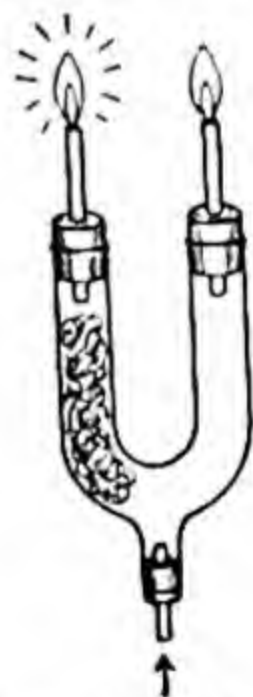


FIG. 293.—LUMINOSITY IMPARTED TO HYDROGEN FLAME BY BENZENE VAPOUR.

and lighting the two jets. The hydrogen saturated with benzene vapour burns with a luminous flame.

Besides gas coke, left in the retorts in gas works and used as fuel, a very hard and compact form of coke is specially made for metallurgical purposes (blast furnaces) by carbonising coal in coke ovens. In the old 'beehive ovens' part of the coal was burnt and the heat produced carbonised the rest, as in charcoal burning. In this way all the valuable by-products (tar, gas, ammonia and benzene) were lost. In the modern 'recovery ovens' (Fig. 294) the coal is heated by gas in narrow fireclay retorts,

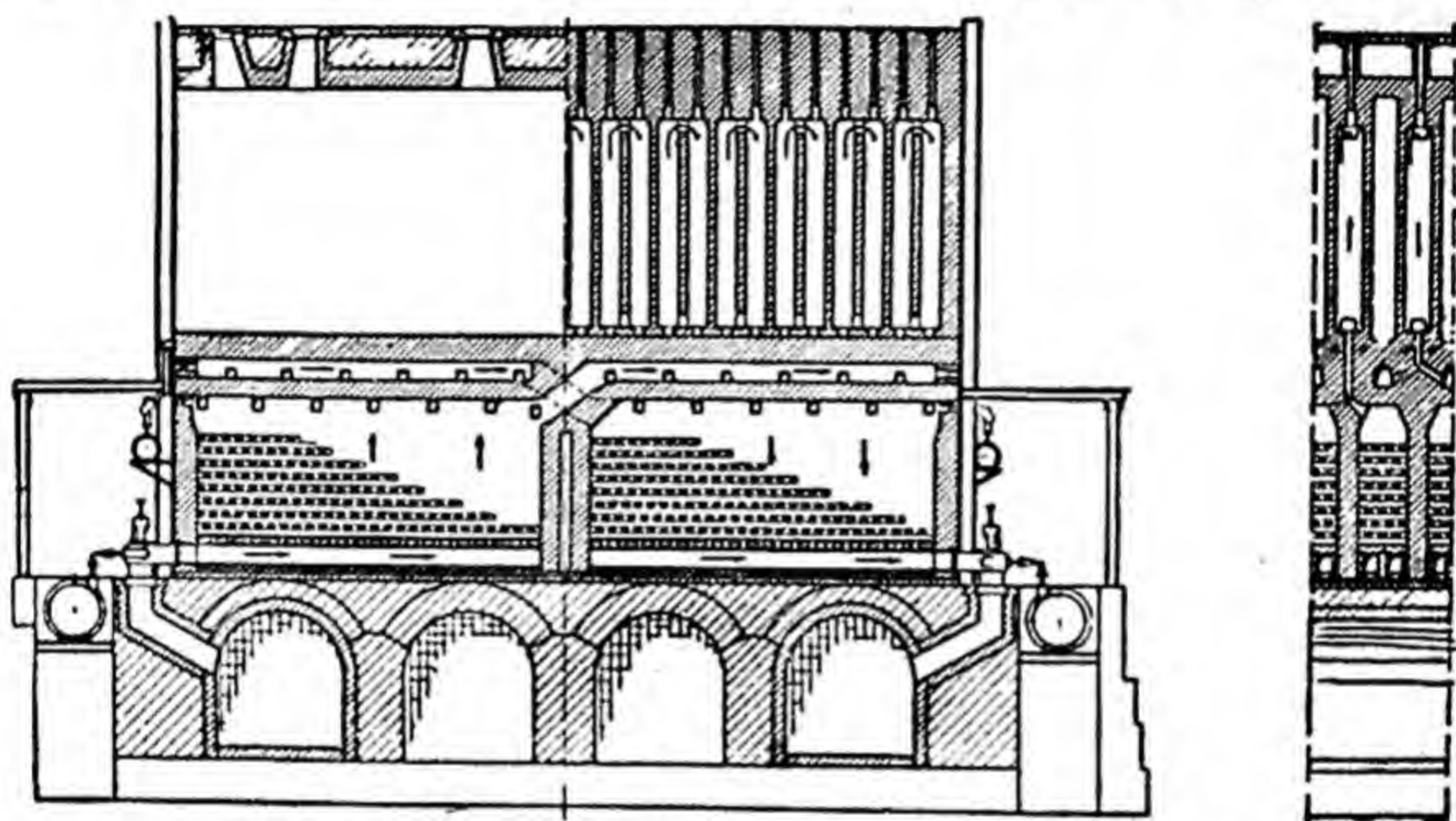


FIG. 294.—BATTERY OF COKE OVENS ARRANGED FOR RECOVERY OF BY-PRODUCTS.

the gases evolved being collected and treated, and the residual coke pushed out by rams and quenched by water. Such *oven coke* is hard enough to stand the weight of the blast furnace charge without crushing down.

**Flame.**—In combustion reactions, *i.e.*, reactions proceeding with the evolution of heat and light, it is usual to distinguish between those attended by ignition only and those attended by the production of flame. An incandescent mass of fuel, such as coke, may burn without flame, but in addition to this there may be flames of carbon monoxide burning on the top of the mass. This example is typical of all others: a flame is produced only during the combustion of gas or vapour, and it may be formally defined as *a zone in which chemical reaction between gases is occurring, attended by the evolution of heat*



*and light.* Flame is produced only in reactions which liberate considerable amounts of energy, sufficient to raise the gas to a very high temperature.

We may next distinguish between luminous and non-luminous flames. A flame of pure hydrogen, burning in dust-free air, emits hardly any visible light (Fig. 295); carbon monoxide burns with a blue flame, but does not emit much light. These are non-luminous flames. The alcohol flame in a spirit lamp and the Bunsen flame are also non-luminous. Ethylene, acetylene, coal gas and candle flames are all luminous flames and emit considerable light (Fig. 296).



FIG. 295.—HYDROGEN FLAME.

The gas inside the flame is usually called the *combustible*, and the gas outside, the *supporter of combustion*, but these terms are relative only, since either gas may be a combustible or a supporter of combustion according to the arrangement of the

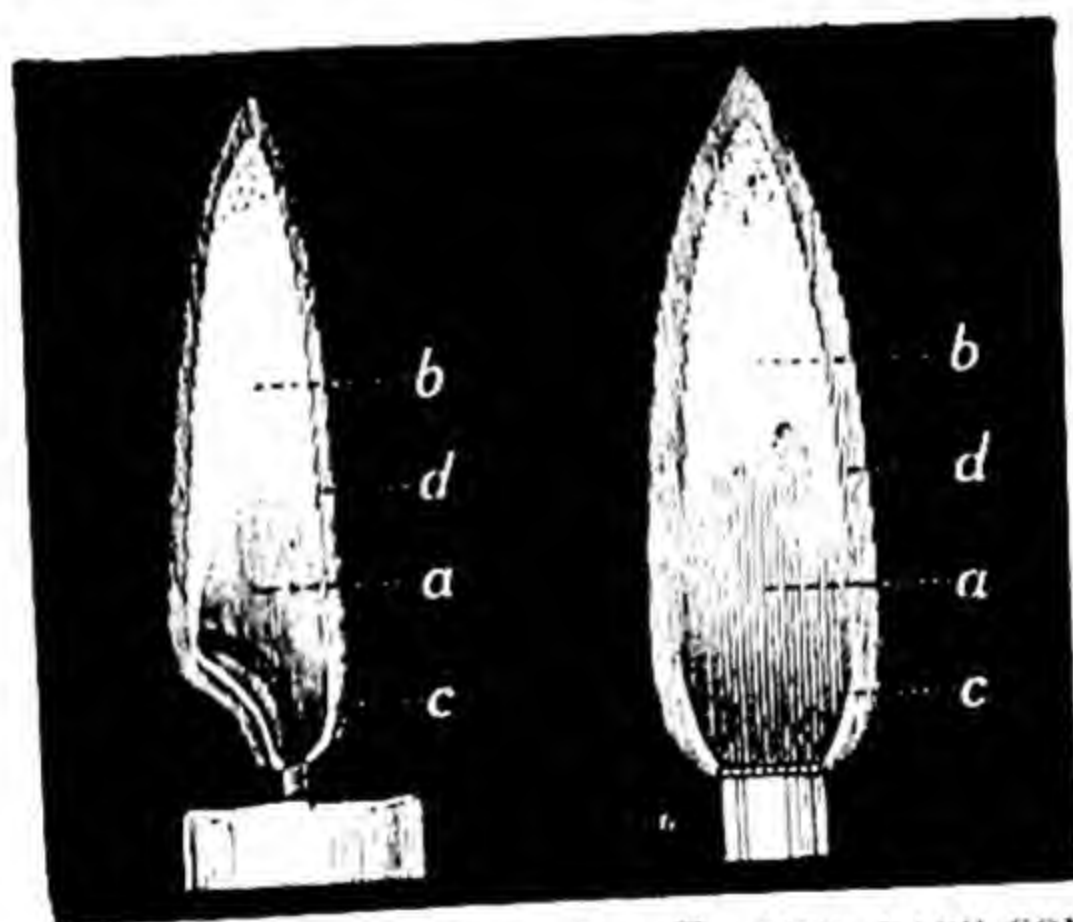


FIG. 296.—CANDLE AND COAL GAS FLAMES, EACH CONSISTING OF FOUR CORRESPONDING PARTS.

method of combustion. Liquids such as paraffin, and solids such as wax, can burn with flame only when they are first converted into gases or vapours, and this is the purpose of the *wick* in the lamp or candle. The oil or melted wax is raised by capillary attraction through the wick and enters the very hot space inside the flame. Here it is decomposed with the

formation of combustible gases or vapours, which then undergo energetic oxidation to produce the flame.

The following are the main *characteristics* of flames, as illustrated by simple experiments.

(1) Unless the combustible gas and the supporter of combustion are first mixed together, the reaction between them will be limited to a region where they come in contact. Thus flames are hollow. This may be exhibited by the following experiments.

A piece of asbestos paper is lowered on a Bunsen flame, when a scorched ring is formed. A match head is thrust quickly inside a Bunsen flame: it does not ignite for a considerable time. One end of a glass tube is inserted inside a Bunsen flame: unburnt gas passes out of the tube and may be kindled at the upper end. The hollow character of flame was demonstrated by Hooke in 1676 by depressing a thin piece of glass on a candle flame: the dark centre of unburnt gas is then seen.

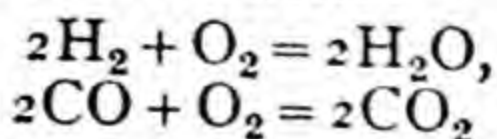
(2) The terms combustible and supporter of combustion are purely relative, and depend simply on which gas is inside and which outside the flame. This has already been illustrated in the case of oxygen and hydrogen (p. 282). Another experiment is as follows.



FIG. 297.—AIR BURNING IN COAL GAS.

A lamp chimney (Fig. 297) is fitted with a cork at the lower end, through which pass a wide straight tube and a narrow tube bent at an angle. Coal gas is passed in through the bent tube, and may be kindled at the top of the glass, burning with a luminous flame. At the same time air is drawn in through the wide tube, and if a lighted taper is passed up through this tube into the chimney, the air ignites and burns in the coal gas with a blue non-luminous flame. If a taper is passed down to the air-flame, it cannot be kindled, since it is surrounded by an atmosphere of coal gas, which will not support combustion of the hydrocarbons of the taper. A jet of air, however, may be ignited.

(3) The structure of flame. A hydrogen or carbon monoxide flame consists of two cones, an inner cone of unburnt gas and an outer cone in which the reactions:





are occurring. A candle or coal gas flame is more complicated. If it is carefully inspected it will be found (Fig. 296) to consist of four parts: (*a*) the dark inner cone of unburnt gas, or vapour of partly decomposed wax; (*b*) a yellowish-white, brightly luminous region, occupying most of the flame; (*c*) a small bright blue region at the base of the flame; (*d*) a faintly luminous outer mantle, surrounding the flame\* completely. If the supply of gas is reduced, the flame shrinks down, the luminous area *b* gradually disappearing, whilst the region *c* becomes continuous, and constitutes an inner cone. The regions *a* and *d* remain.

The structure of a candle flame is shown by the following experiment. A bent glass siphon is lowered into the flame

(Fig. 298). With the tube just above the wick, dense white vapours pass over into the flask: these correspond with the first process in the flame, the volatilisation of the solid wax by the heat, which occurs on the wick in the dark central portion of the flame. On raising the tube into the bright central portion of the flame, dense black vapours pass over, containing particles of solid carbon produced by the decomposition of hydrocarbons by the heat of the flame. The presence

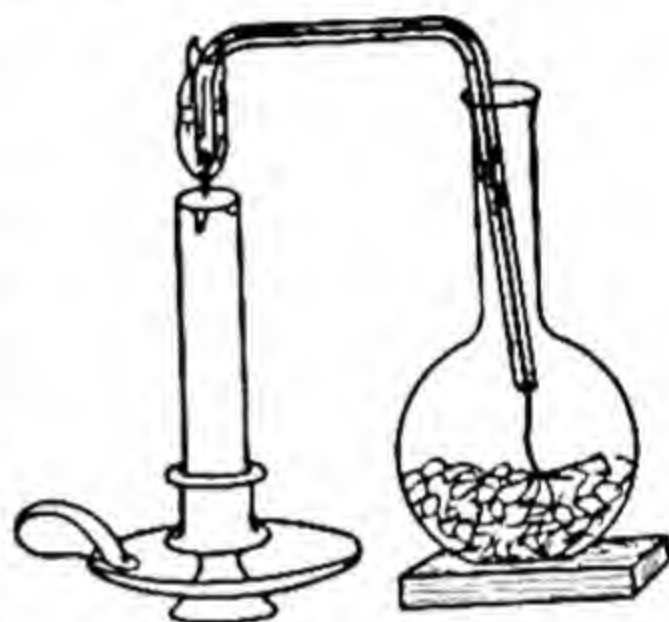


FIG. 298.—EXPERIMENT TO ILLUSTRATE THE STRUCTURE OF A CANDLE FLAME.

of these fine particles of carbon, raised to incandescence, is probably the cause of the luminosity of the flame. Some luminous flames (*e.g.*, of arsenic in oxygen) cannot contain solid particles.

**Davy's investigations on flame.**—Sir Humphry Davy in 1815 was led to the study of flame by an investigation of the causes and prevention of fire-damp explosions in coal mines, which were prevalent when open candle flames were used. These are caused by the ignition of mixtures of methane (*fire-damp*) and air; or, as we now know, sometimes by the kindling of a mixture of very fine coal dust itself with air. Davy made the discovery that if a flame is cooled it is extinguished, and he recognised that combustible gases have different **ignition points**.

The ignition point of methane is rather high, so that it is not kindled by red-hot metal.

If a piece of fine wire gauze is lowered over a Bunsen flame,

this at first does not pass through the gauze, owing to the cooling effect caused by conduction of heat through the metal, and a red-hot ring is seen on the gauze, with a dark patch in the centre



FIG. 299.—PRINCIPLE OF SAFETY LAMP.

corresponding with the central unburnt portion of gas in the flame. If the gauze is allowed to remain on the flame a sufficiently long time, the temperature of the metal rises to the ignition point, when the gas ignites and burns above the gauze.

If a piece of gauze, turned up at the edges, is held over an unlighted gas burner, the gas passing through may be kindled above the gauze, but the flame does not pass through and light the gas at the burner. On raising the gauze, the flame flickers and finally goes out (Fig. 299). This flame, in which air is mixed with gas before combustion, is blue and non-luminous.

These experiments led Davy to the invention of the safety lamp, which consists of an oil lamp having an enclosed cylinder of wire gauze as a chimney (Fig. 300). The fire-damp will penetrate inside the gauze and burn there, but the flame does not pass outside, because the heat is conducted away by the metallic gauze. The gauze may even become red-hot, but as the ignition temperature of methane is high, the gas outside is not kindled. A draught of air blowing on the lamp may cause the gauze to become so hot as to ignite the fire-damp, and the flame inside may also be blown mechanically through the gauze by a blast of air, caused by firing a shot. With these exceptions the lamp, in its improved form, with a strong glass cylinder below the gauze, which permits of better illumination, is perfectly safe.

**The Bunsen flame.**—The experiments just described show that if coal gas is mixed with a sufficient supply of air *before*

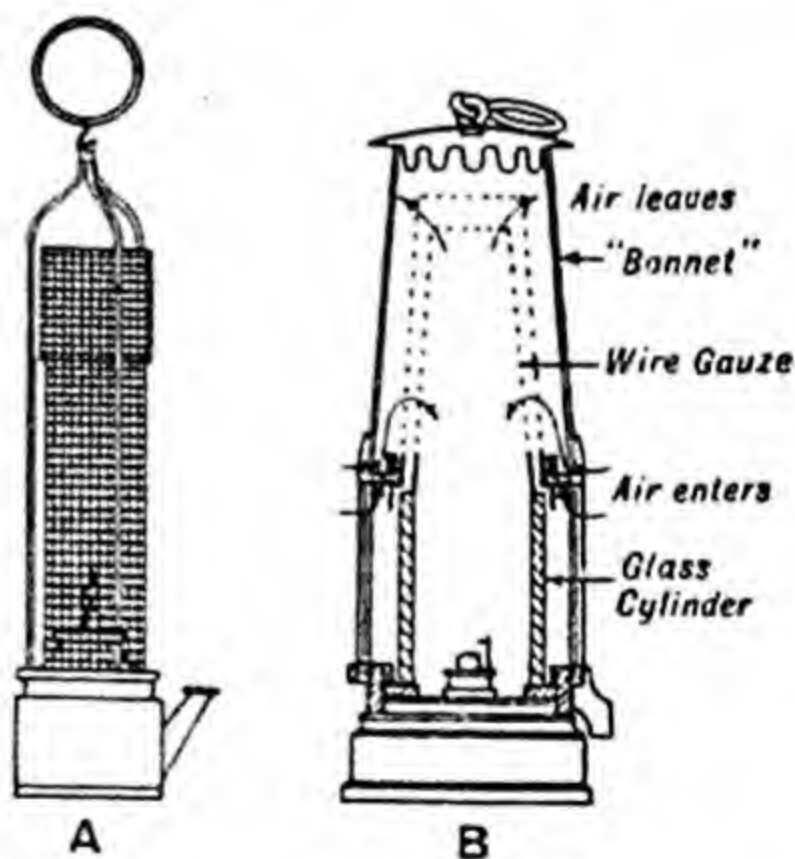


FIG. 300.—DAVY'S SAFETY LAMP.



combustion it burns with a non-luminous flame, as in the familiar Bunsen burner.

The **Bunsen burner** consists of a small jet bringing in a stream of coal gas, over which is placed a wider metal tube with holes opposite the inner jet. The coal gas passing out of the jet produces a reduction of pressure, air streams in through the holes in the outer tube, and mixes with the gas. The mixture of gas and air is ignited at the top of the tube. The Bunsen flame consists of two cones only: (1) a pale blue inner cone, which becomes green when a large supply of air is admitted, and the flame 'roars'; (2) a still paler blue outer cone. The reactions in the inner cone are different from the purely thermal decompositions taking place in an ordinary flame, since partial oxidation now occurs, with formation of carbon monoxide. This burns in the outer cone.

The separation of the two cones of a Bunsen flame is most conveniently effected by means of **Smithells' flame-cone separator**. This consists (Fig. 301) of one glass tube sliding inside a wider tube. A mixture of air and gas from a Bunsen burner is passed into the central tube. By raising the outer tube the flame separates into two cones, one of which remains on the outer tube, and the other, which is the inner cone of the complete flame, burns on the top of the narrower tube. By raising the latter, the inner cone may be joined to the outer one, and the complete flame produced.

The Bunsen flame is utilised in a great number of everyday appliances making use of gas. The burners used for heating the incandescent mantles in gas lighting, and those in gas stoves and gas furnaces, are of this type. The only drawback is the tendency to 'strike back' when the supply of gas is reduced below a certain limit. The rate of supply must be sufficient to prevent the combustion, which travels through the mixture of air and gas at a certain rate, from running down the tube, when the undiluted gas ignites at the small jet supplying it to the burner, causing the burner to become very hot, and also producing incompletely burnt gas with an unpleasant odour

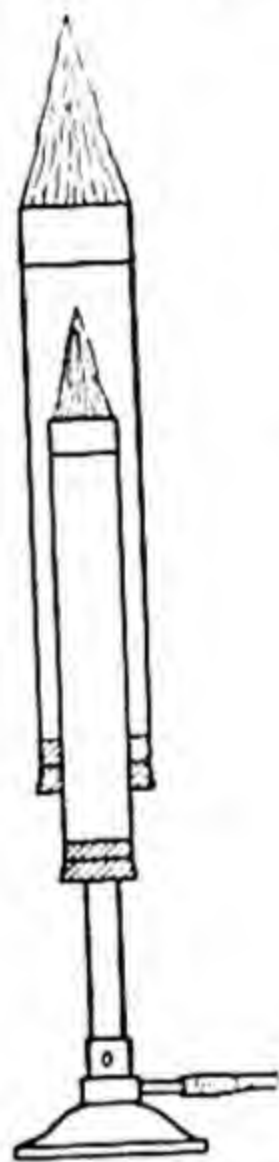


FIG. 301.—SMITHELLS' APPARATUS.

(p. 441). The striking back may be avoided by covering the top of the burner with metal gauze, through which the flame cannot pass. This is done in some modern gas stoves. In gas furnaces, a blowpipe type of burner is used, the air being supplied under pressure and mixing with the gas just as the latter is burnt. The blowpipe consists of two concentric metal tubes (Fig. 188), the air being supplied through the inner tube. The mechanical action of the blast causes better thermal contact with the object to be heated.

**\*Explosion.**—When a mixture of inflammable gas with oxygen or air is ignited, the mixture burns with great rapidity, and if the ignition is made in an open vessel there is usually a report called an explosion. It was found by Berthelot, Dixon, and others that an explosion *starts* with much less violence than is exhibited in its final stages, and that the flame runs through the gas at first with a fairly low speed. At a certain point the speed of the flame suddenly increases enormously, and flame rushes through the gas in the form of a **detonation wave**, travelling with great velocity and capable of exerting great destructive action.

Dangerous explosions (detonations) may also be caused by the ignition of fine **combustible dust** dispersed in air. For example, very bad explosions have been caused in collieries by fine coal dust, and in flour mills by fine flour dust. In small quantities such mixtures would be scarcely combustible, but once a detonation wave has been initiated in them, it propagates itself with terrible violence. In 'dusty' mines, powdered stone ('incombustible dust') is laid down either by spades or by a special blower, so that it becomes stirred up by a disturbance and damps out the explosion. The incombustible dust, which must not contain silica, must form 50 per cent. of the dust taken from any part of the mine.

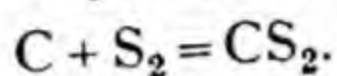
In gas or petrol engines a compressed mixture of gaseous or 'atomised' fuel and air is ignited, usually by an electric spark, in the cylinder. The burning of the mixture produces a high temperature and a rise of pressure, which is made use of in driving the piston down the cylinder. The burnt gas is then driven out through an exhaust valve, which opens when the piston is nearly at the bottom of its stroke, and the rest is pushed out by the rise of the piston. During the next descent of the piston a fresh charge of mixture is drawn in through the inlet valve (with the exhaust valve closed), and this is compressed in the next upward motion of the piston, both valves being closed.



The compressed gas is then fired as the piston approaches the top of its motion, and the cycle is begun anew. In the Diesel engine the ignition is brought about by the high temperature produced by compression of the air in the cylinder, oil being then sprayed into the heated air.

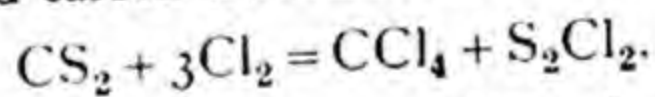
The normal process of combustion in the engine cylinder is *not an explosion* in the usual sense. It is a *rapid burning* of the mixture, with the production of a high temperature and pressure rise.

**\*Carbon disulphide.**—When sulphur vapour is passed over red-hot carbon, carbon disulphide (or 'bisulphide'),  $\text{CS}_2$ , a volatile, very inflammable liquid is formed :



As usually prepared, this has a most unpleasant smell, but when perfectly pure it has an ethereal odour, which becomes unpleasant when the liquid is kept for a short time. The vapour has a very low ignition temperature : it is kindled by a test-tube filled with hot oil. It forms an explosive mixture with oxygen or air, and a combustible mixture with nitric oxide (p. 393). The vapour is used in killing insects, and rats in grain stores. The liquid dissolves sulphur, white phosphorus, rubber, camphor, resin, oils and fats, and is used as a solvent. It is poisonous.

Carbon disulphide on chlorination yields sulphur chloride (boiling point  $138^\circ$ ) and carbon tetrachloride,  $\text{CCl}_4$  (boiling point  $77^\circ$ ) :



Carbon tetrachloride is used as a solvent for fats, etc., and for extinguishing fires ('pyrene,' p. 416).

## CHAPTER XXVI

### PHOSPHORUS. SILICON. BORON

**Phosphorus.**—Although without matches we should now feel greatly inconvenienced, these useful and time-saving articles have been in existence only about a century. The flint and steel, a relic of prehistoric man, was relegated to the museum by the application of the chemical element phosphorus, which had been known a century and a half before this use was discovered. Phosphorus in the free state serves for the manufacture of matches; combined phosphorus is an essential fertiliser and a constituent of food. Animal and vegetable tissues, especially in seeds, the yolk of eggs, the nerves and brain, and bone marrow, contain phosphorus usually in the form of complicated fats known as *lecithins* or *glycerophosphates*. In the life-processes these are broken up, and phosphoric acid excreted through the agency of the kidneys in the form of salts. It is an essential constituent of bones in the form of calcium phosphate. During the first year of its life an infant requires about 50 to 60 grams of phosphorus, and much more than this must be taken in with the food, because some phosphorus is continually excreted. It is a remarkable fact that human milk contains much less phosphorus than cow's or goat's milk, but the amount is sufficient because the child's development occurs more slowly than is the case with most mammals.

Plants take up phosphorus from the soil in the form of calcium phosphate, which dissolves in water containing carbonic acid, and materials containing calcium phosphate, such as bone-meal, basic slag, and superphosphate of lime are valuable fertilisers.

**History of phosphorus.**—About 1674, Brand of Hamburg obtained phosphorus by distilling evaporated urine, which contains phosphates, and carbon. It had the property of shining in the dark and hence was called phosphorus



(Greek *phos* = light; *phero* = I bear). Krafft exhibited phosphorus at the Court of Charles II (a monarch interested in science, and the patron of the Royal Society) in 1677. It was seen by Robert Boyle, and the method of preparation was rediscovered by him in 1680, although Kunckel had also found out the process in Berlin two years previously. Gahn, in Sweden, about 1770, discovered that bones contain a large quantity of calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , and Scheele prepared phosphorus from bone ash. It was recognised as an element by Lavoisier in 1777. Phosphorus was made for sale in London from the time of Boyle's discovery by Ambrose Godfrey Hanckwitz, who had a laboratory near the Strand which was a fashionable resort for those interested in experiments. Previous to Scheele's discovery, the element was very rare and expensive. The annual production of phosphorus now amounts to about 5,000 tons, most of it being used for matches.

**Occurrence of phosphorus.**—Phosphorus occurs always in the combined state and mainly as phosphates. The primary mineral is probably *apatite*,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ , a fluoride and phosphate of calcium, in which part or all the fluorine may be replaced by chlorine. The name is derived from the Greek *apatao* = I deceive, since early mineralogists often confused the mineral with others. From apatite, secondary deposits of phosphates, such as calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ ; aluminium phosphate,  $\text{AlPO}_4$ ; and ferric phosphate,  $\text{FePO}_4$ , may have been formed. These are used in the production of phosphorus.

Animal bones in the fresh condition contain over half their weight of calcium phosphate, together with some calcium carbonate, fat, and organic matter containing nitrogen. The fat may be extracted with carbon disulphide, the organic matter dissolved as gelatin or glue by heating with water under pressure, and the residue heated in closed retorts to form *animal charcoal* or *bone black*, used for decolorising sugar. When no longer active, this is heated in air to burn off carbonaceous matter, and *bone ash*, consisting chiefly of calcium phosphate, with some carbonate, remains. This may be used to prepare phosphoric acid (*q.v.*).

**Preparation of phosphorus.**—Phosphate minerals, such as calcium phosphate, are broken up and mixed with sand and coke. The mixture is fed into an electric furnace (Fig. 302) containing two carbon rods between which an electric arc is struck, producing a very high temperature, but no electrolysis

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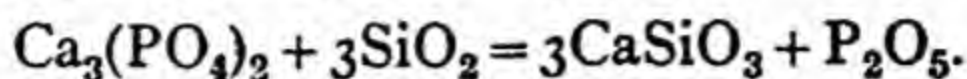
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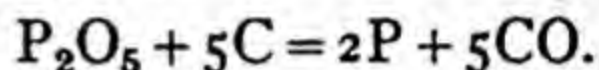
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(*cf.* aluminium). The silica of the sand displaces phosphoric oxide from the phosphate, forming calcium silicate :



The vapour of the phosphoric oxide is reduced by the carbon at the very high temperature, carbon monoxide and phosphorus vapour being formed :



The phosphorus vapour is condensed by cooling, and the solid purified by melting under a solution of chromic acid, after which it is cast into wedges or sticks of white phosphorus, the common form.

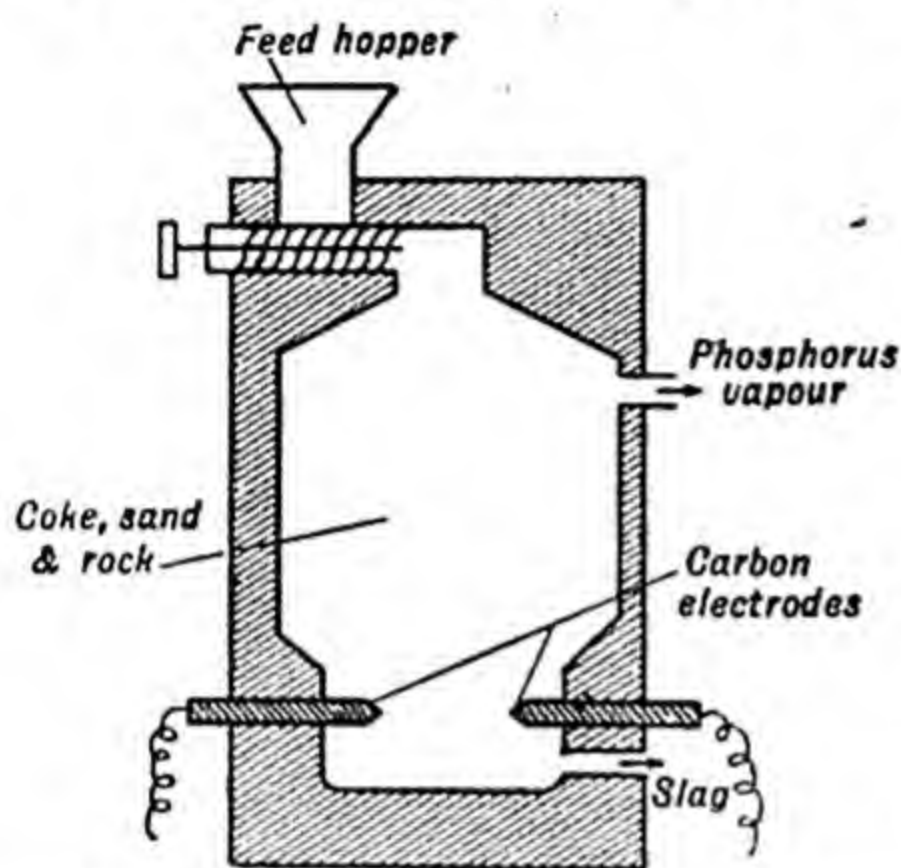


FIG. 302.—INDUSTRIAL PREPARATION OF PHOSPHORUS BY HEATING A MIXTURE OF A MINERAL PHOSPHATE, SAND, AND COKE, IN THE ELECTRIC FURNACE.

**Allotropic forms of phosphorus.**—Phosphorus exists in two common allotropic forms :

(1) **White phosphorus**, sometimes incorrectly called 'yellow phosphorus' (it is perfectly white when pure and turns yellow only after exposure to light). This is the common, very inflammable, form.

(2) **Red phosphorus**, sometimes incorrectly called 'amorphous phosphorus' (it is really crystalline).

**White phosphorus.**—White phosphorus is a translucent white solid, rather like paraffin wax in appearance. It is soft at room temperature and is easily cut with a knife, an operation which should always be performed under water since this form of phosphorus ignites in air at about  $50^\circ$ , and this temperature may be reached locally by the friction of cutting, or merely by the spontaneous oxidation of the phosphorus. White phosphorus has a low melting point ( $44^\circ$ ) but a high boiling point ( $287^\circ$ ). The vapour density shows that the vapour contains the molecule  $\text{P}_4$ , which is also present in solutions. Phosphorus is only very slightly soluble in water ; it dissolves more readily in ether, olive oil, and benzene, and it is very soluble in carbon disulphide. By the slow evaporation of the solution in carbon disulphide out of contact with air and in the dark, large



transparent crystals are deposited, which exhibit a play of colours like that of the diamond. These are also formed by subliming phosphorus in a vacuum tube.

White phosphorus is very easily oxidised and is always kept under water. On exposure to air at room temperature it undergoes spontaneous oxidation, accompanied by a green glow or phosphorescence, and the emission of fumes with a characteristic odour. At about  $50^{\circ}$  it catches fire in air, burning with a brilliant white flame and forming white fumes of phosphorus pentoxide,  $P_2O_5$ . A residue of red phosphorus also remains. Finely divided white phosphorus, left after the evaporation of the solution in carbon disulphide, ignites spontaneously in air, and fused phosphorus burns under water in a current of oxygen.

The glow of phosphorus is strikingly shown in the following experiment ('the cold flame'). A few pieces of dry phosphorus are placed in a receiver, which is then filled up with glass wool. The receiver is heated gradually on a water bath, a stream of carbon dioxide being passed through (Fig. 303). The phosphorus vapour carried along with the gas oxidises in the air, and a green flame appears at the top of the exit tube. This is so cool that the hand may be held in it, and it will not kindle the head of a match.

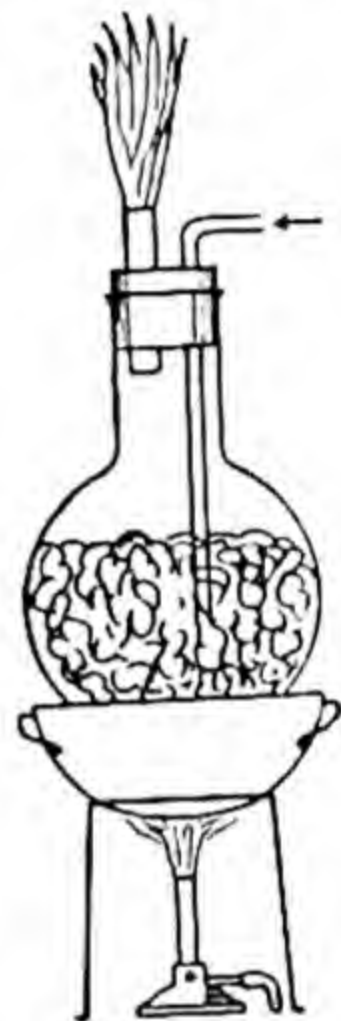


FIG. 303.—THE 'COLD FLAME.'

The French chemist, Lemery, who wrote a very popular text-book (*Cours de chimie*, 1st ed. 1675, which sold, we are told in the last edition, 1756, 'comme un ouvrage de galanterie ou de satire'), quotes an amusing example of the ready inflammability of phosphorus. 'After some experiments on phosphorus had one day been made in my house, a small piece of it was left by oversight on the bedroom table. The servant, in making the bed, lifted it up, without seeing it, in the sheets which she had placed on the table. The occupant of the bed, being awakened in the night, probably on account of his feeling some heat, observed that the coverlet was on fire. In fact, the phosphorus, having been affected by the heat of the occupant of the bed, had set fire to the coverlet and had already burnt a large hole in it.'

Phosphorus catches fire at once when sprinkled with iodine, iodides of phosphorus,  $PI_3$  and  $P_2I_4$ , being formed.

'Phosphorescence' is not confined to the slow oxidation of phosphorus. Some compounds, such as calcium sulphide containing traces of bismuth or other heavy metals, shine in the dark after exposure to bright light. This is a purely physical phenomenon. Phosphorescence is also exhibited by chemical reactions: a little ether dropped on a hot plate undergoes oxidation and phosphoresces. The light of fireflies is due to the oxidation of a substance called *luciferin* by an enzyme, *luciferase*.

It is curious that, although the phosphorescence of phosphorus is due to oxidation, the element does not glow in pure oxygen at the ordinary temperature and pressure. When the pressure of the oxygen is reduced, phosphorescence begins. The glow of phosphorus in air is stopped by the vapours of some essential oils, such as turpentine.

White phosphorus is very *poisonous*, the lethal dose being about 0.15 gm. Workmen exposed to the vapour are liable to decay of the bones, especially of the jaw, and its use in the manufacture of matches has ceased.

**Red phosphorus.**—The second common form of phosphorus, discovered by Schrötter in 1845, is red phosphorus. It is produced by heating white phosphorus in an inert atmosphere (nitrogen or carbon dioxide), when transformation occurs, accompanied by a considerable evolution of heat. It is also left as a residue when white phosphorus burns in air. Red phosphorus is prepared by heating fused white phosphorus in a large cast-iron pot provided with a cover through which passes an upright iron tube. The temperature must be carefully controlled at about  $230^{\circ}$ . A little phosphorus burns, absorbing the oxygen from the air of the vessel, and the rest slowly solidifies to a mass of red phosphorus. This is ground up under water, boiled with caustic soda solution to free it from unchanged white phosphorus, washed and dried. It forms a violet-red-coloured powder.

Red phosphorus is not self-luminous, has no smell or taste, and is not poisonous. It is insoluble in carbon disulphide or hot caustic alkali solution. On exposure to air it undergoes very little change, although there is slight oxidation and the mass becomes moist. It does not ignite in air until heated to about  $240^{\circ}$ . When strongly heated it is converted into vapour, which condenses on cooling in the form of white phosphorus. This may be shown by heating a little red phosphorus in a hard glass tube through which a current of carbon dioxide is passing. The



solid volatilises without melting, and colourless drops of white phosphorus condense on the cool part of the tube.

White phosphorus is an unstable form; it is always passing slowly into the stable form, which is red phosphorus. The change is accelerated by heating or by exposure to light. The two forms of phosphorus differ in stability from the two crystalline forms of sulphur (p. 344). Whereas there is a transition temperature in the case of sulphur, below which one form is stable and above which the other becomes the stable form, in the case of phosphorus *the white form is unstable at all temperatures*. The chemical identity of white and red phosphorus may be established by converting equal weights of the two forms into some compound, such as phosphorus pentoxide or phosphorus trichloride, when equal weights of the same compound will be obtained.

**\*Matches.**—Although the production of fire by friction between pieces of wood ('fire drill') and by the use of sparks abraded



FIG. 304.—FLINT AND STEEL, TINDER BOX AND SULPHUR MATCHES.  
ENGLISH TINDER PISTOL, EARLY NINETEENTH CENTURY  
(Bryant and May Museum, London.)

from steel by striking with flint is a prehistoric invention, the use of matches dates back only about a century. A 'flint and steel,' as used generally for kindling fire until the beginning of the nineteenth century, is shown in Fig. 304. A particular kind of *tinder* used to receive the spark was *amadou*, or 'German tinder,' made from a fungus (*Fomes*). Charred rags were commonly used in Great Britain. These were contained in the metal tinder box, and served to ignite splinters of wood tipped with sulphur.

The tinder pistol, introduced during the seventeenth century on the Continent but never much used in Great Britain, is also shown on the left in Fig. 304. The flint and steel were operated by a trigger, and the sparks ignited a piece of tinder.

In 1805 Chancel made use of the discovery of Pelletier in 1789 that a mixture of potassium chlorate and sugar is ignited in contact with concentrated sulphuric acid (see p. 328). Chancel used wooden strips, one end of which was covered with a mixture of potassium chlorate, sugar and gum; this was inflamed by dipping into a small bottle containing asbestos soaked in sulphuric acid. One of these 'Instantaneous Light Boxes,' in which the phial of acid is in the centre, is shown on the right

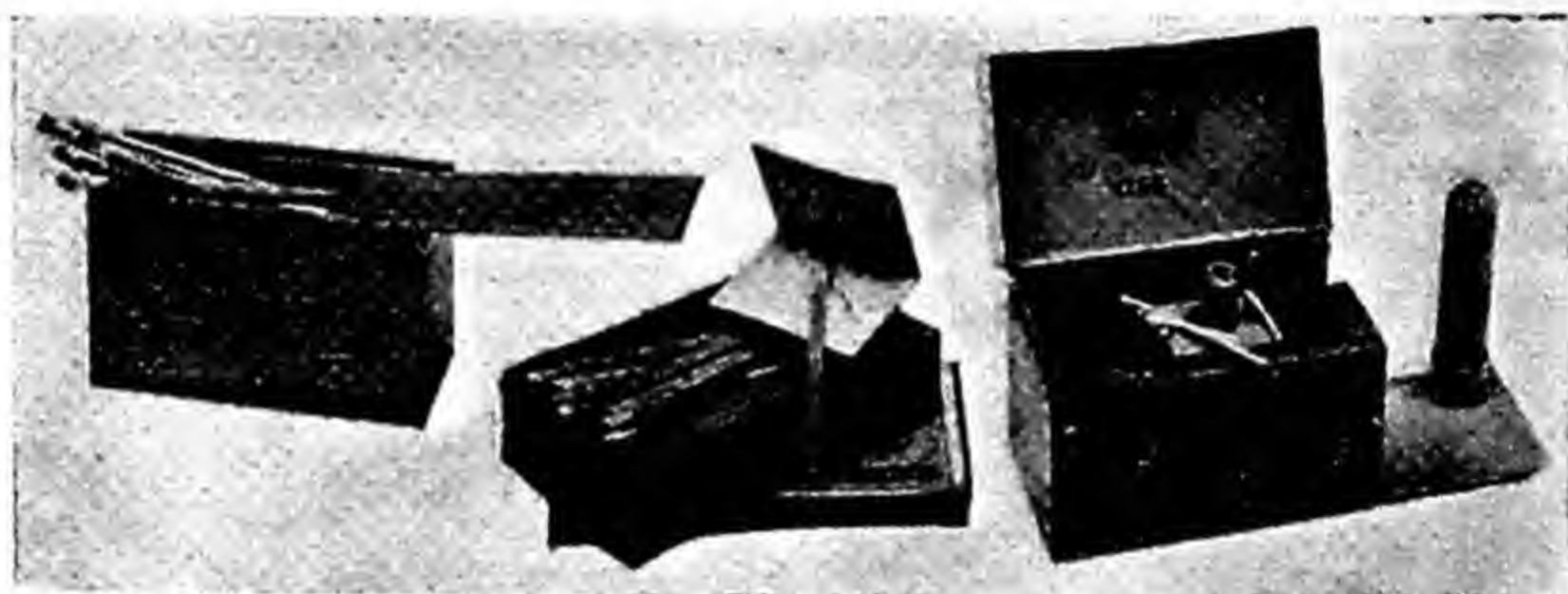


FIG. 305.—INSTANTANEOUS LIGHT BOX, LUCIFERS, AND CONGREVES.

(Bryant and May Museum, London.)

in Fig. 305: it is of English make, and its use was introduced from France about 1810. This appliance was in use for nearly a quarter of a century.

The invention of friction matches is claimed for John Walker, a druggist of Stockton-on-Tees, who in 1826 used matches with heads composed of potassium chlorate, antimony sulphide and gum, at the end of flat wooden splints. To ignite these, the head was placed between folds of sandpaper, nipped tightly between the fingers, and the match suddenly and forcibly withdrawn. A very few of these original 'friction lights' are known to exist.

Walker's idea was appropriated by Samuel Jones of London, who had previously invented a *Promethean Match*, consisting of a tiny vesicle of glass containing a drop of concentrated sulphuric acid and surrounded by a mixture of potassium chlorate, sugar and gum, the whole attached to a paper spill. The vesicle was broken by a blow, or by nipping



between the teeth or the jaws of a small pair of pliers, and the mixture ignited. Jones sold his imitation of Walker's matches under the name of *Lucifers*. A box of Jones's lucifers is shown in the centre in Fig. 305. On the left is a box of an early phosphorus match, *Congreves*, made in Germany about 1835 and with the initials J. C. K., i.e. J. C. Kammerer, of Ludwigsburg in Württemberg, who is said to have invented the phosphorus match, although the label on the box states that the matches were 'invented and improved by Congreve.' Congreve, however, died in 1828, and these matches did not appear until about 1832.

The first use of phosphorus for matches is said to be due to a young French student, Charles Sauria, in 1830. The development of the idea is due to Kammerer in Germany and Siegel in Austria: a patent for phosphorus matches was taken out by Phillips in America in 1836. The heads of these early phosphorus matches consisted of a dried paste of white phosphorus, potassium chlorate and gum. They were ignited by rubbing them on the box or any hard substance. They operated rather explosively, and the chlorate was later replaced by red lead or manganese dioxide. In 1855 'safety' matches were invented in Sweden: the head contains no phosphorus, but antimony sulphide with oxidising agents (potassium chlorate, potassium dichromate, and red lead). This is rubbed on a strip of paper coated with red phosphorus, attached to the box. In many parts of Great Britain, the British Dominions and N. and S. America 'heads' containing phosphorus sulphide,  $P_4S_3$ , which ignite by friction, are used. These "Strike-Anywhere" matches were originally prepared with yellow phosphorus, but have for many years been manufactured universally with the sulphide, which is non-poisonous.

In the modern manufacture of matches the wooden splints are first impregnated with salts to prevent the wood glowing when the match is extinguished, and are dried. The splints are then fed mechanically into holes in a very long travelling band, any portion of which with the splints attached and hanging downwards, looks like a hair brush with very coarse bristles. The splints pass through a bath of melted paraffin wax, and the lower ends of the splints then pass over a roller on which a layer of the match-head composition in a viscous condition is maintained. The tipped splints then proceed with the travelling band over a number of large wheels, in which process they are dried. They finally return to the place

where they started, where they are automatically knocked out of the holes in the band and packed in boxes (Fig. 306). Each machine turns out 5,000,000 matches a day, and Bryant and May's factories produce about 90,000,000,000 matches annually.

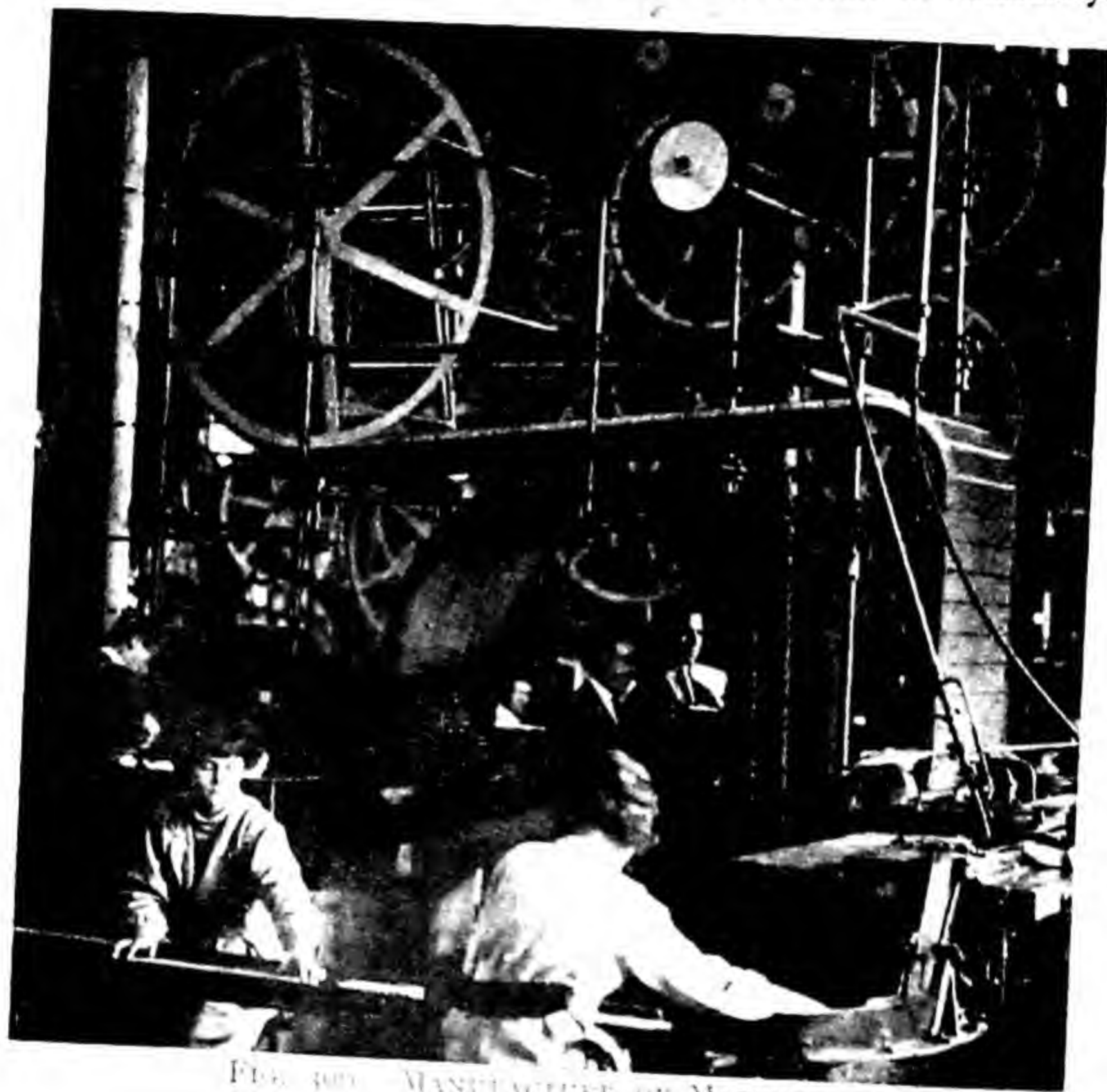


FIG. 306. MANUFACTURE OF MATCHES.  
(Bryant and May, London.)

**Phosphine or phosphoretted hydrogen.** Phosphorus belongs to the same group of elements in the periodic system as nitrogen, and it forms a compound with hydrogen which is analogous to ammonia,  $\text{NH}_3$ , viz. trihydrogen phosphide,  $\text{PH}_3$ , commonly called phosphine or phosphoretted hydrogen. Like ammonia this shows basic properties, but much more feebly, and with dry halogen acids (not with oxyacids) forms phosphonium salts, analogous to ammonium salts. The most stable of these is phosphonium iodide,  $\text{PH}_4\text{I}$ .



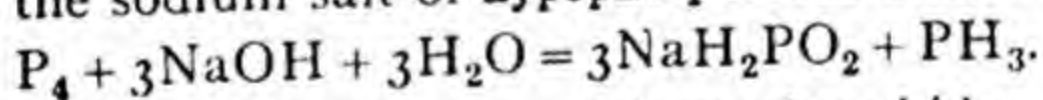
Phosphine was discovered by the French chemist Gengembre in 1783, by heating white phosphorus with a solution of caustic potash. He found that it was spontaneously inflammable, but this property was shown by Thenard in 1845 to be due to the presence of a small quantity of the vapour of a liquid hydrogen phosphide ( $P_2H_4$ ) in the phosphine: *pure* phosphine is not spontaneously inflammable.

Phosphine is prepared :

(1) By heating pieces of white phosphorus in a flask with a strong solution of caustic soda. The air (which would form a spontaneously explosive mixture with the gas)

is first swept out by a current of coal gas (Fig. 307). The phosphine evolved may be allowed to bubble through a trough of water in a fume cupboard. Each bubble ignites spontaneously with a bright flash, and a vortex ring of white smoke, consisting of phosphorus pentoxide, rises if the air is still. The reaction produces phosphine and a solution of sodium hypophosphite,

$NaH_2PO_2$ , the sodium salt of hypophosphorous acid,  $H_3PO_2$  :



(2) By the action of water on calcium phosphide :

$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$ , a spontaneously inflammable gas is produced (Fig. 308). Calcium phosphide is obtained by passing phosphorus vapour over heated quicklime. Tin canisters filled with calcium phosphide, attached to wooden floats, are sometimes used at sea for signalling. The canister is pierced above and below and thrown overboard. The gas ignites spontaneously and burns with a luminous flame (Holmes's signal).

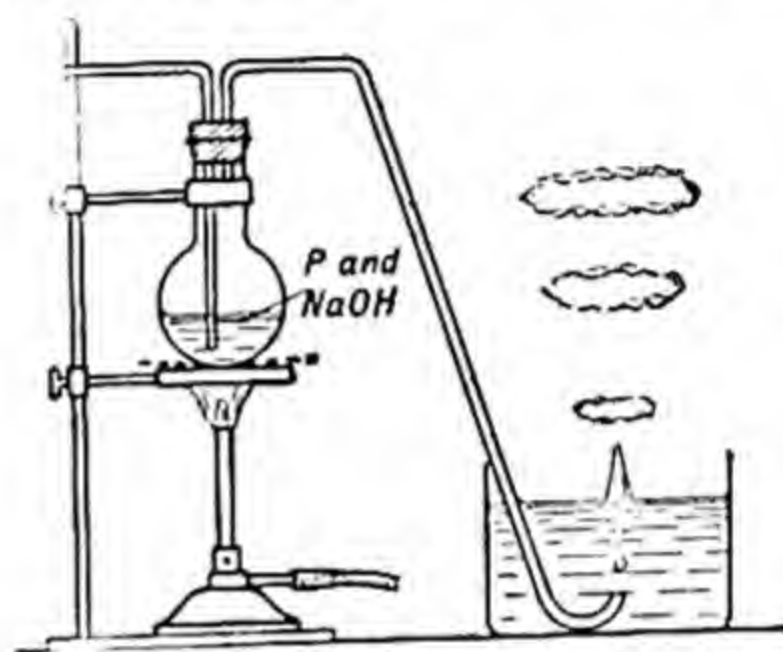


FIG. 307.—PREPARATION OF PHOSPHINE BY HEATING WHITE PHOSPHORUS WITH CAUSTIC SODA SOLUTION.

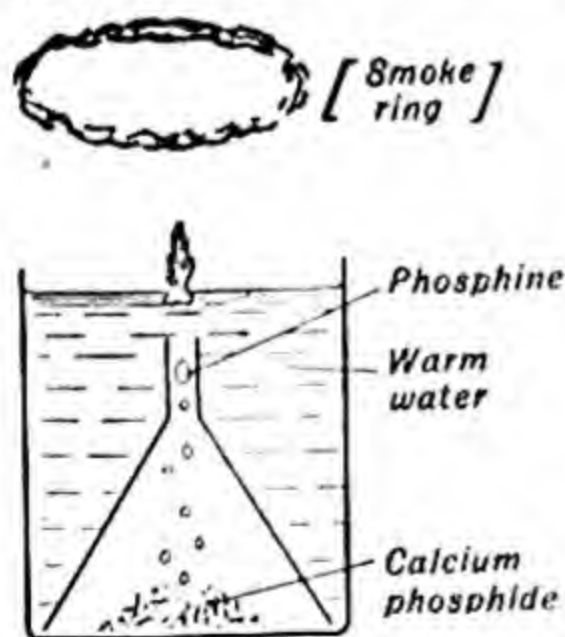
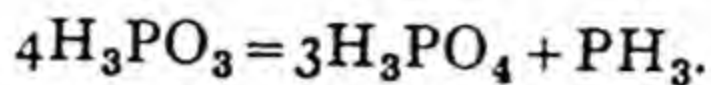
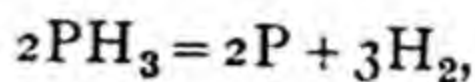


FIG. 308.—ACTION OF WATER ON CALCIUM PHOSPHIDE.

(4) Pure (not spontaneously inflammable) phosphine is obtained by heating phosphorous acid,  $\text{H}_3\text{PO}_3$  :



Phosphine is a colourless gas with a most unpleasant odour of decaying fish, is poisonous, and is only sparingly soluble in water. It is decomposed by heat or electric sparks into red phosphorus and hydrogen :



and its composition may be determined in this way.

Unless perfectly pure, phosphine ignites spontaneously in air. A mixture of *pure* phosphine and oxygen is not spontaneously inflammable, but if the pressure is reduced a violent explosion occurs. The gas ignites spontaneously in chlorine. It precipitates phosphides from solutions of salts of heavy metals, such as copper sulphate. These are also formed by boiling white phosphorus with the solution of the salt of the metal.

**Chlorides of phosphorus.**—White or red phosphorus combines spontaneously with chlorine to form two compounds :

phosphorus trichloride,  $\text{PCl}_3$  (liquid),  
phosphorus pentachloride,  $\text{PCl}_5$  (solid).

The trichloride is prepared by passing a slow stream of dry chlorine over white or red phosphorus heated in a retort and

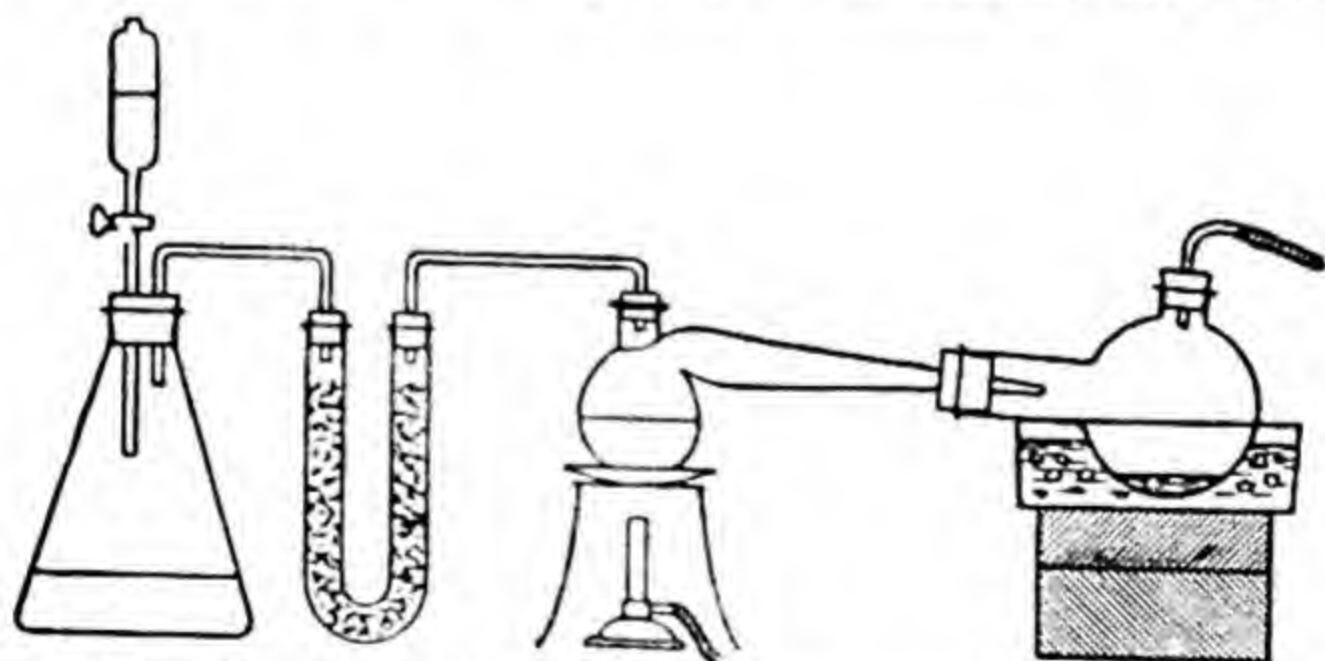
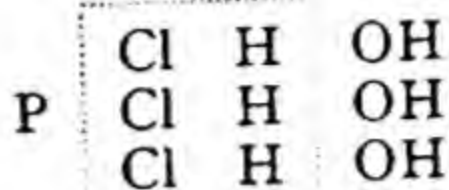
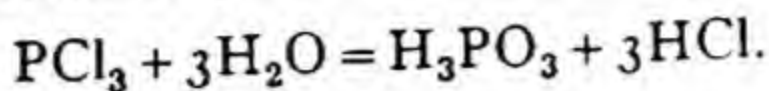


FIG. 309.—PREPARATION OF PHOSPHORUS TRICHLORIDE BY PASSING CHLORINE OVER PHOSPHORUS.

collecting the chloride in a well-cooled receiver (Fig. 309). It is a colourless, strongly fuming liquid, which in contact with

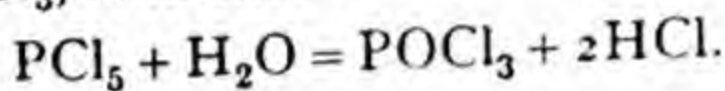


water is *hydrolysed* into hydrochloric acid and phosphorous acid,  $\text{H}_3\text{PO}_3$ :

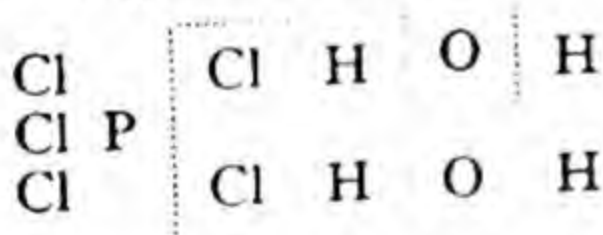


The pentachloride is prepared by the action of chlorine on the trichloride, say by dropping the latter into a cooled flask through which a stream of chlorine is passing (Fig. 310), or by the action of excess of chlorine on phosphorus. It is a white solid which fumes in air and is hydrolysed by water *in two stages*:

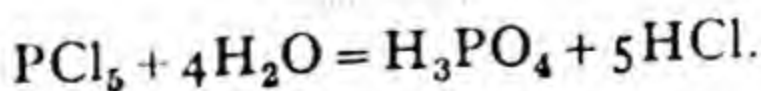
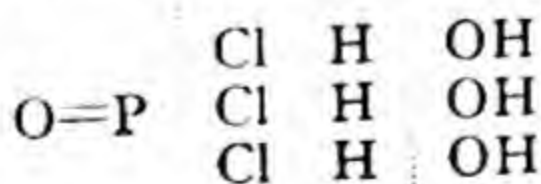
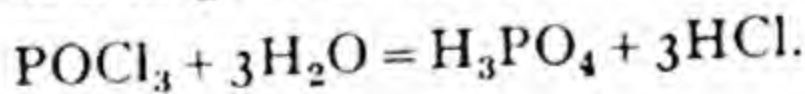
(i) With a *limited amount of water*, a volatile liquid, phosphorus oxychloride,  $\text{POCl}_3$ , is formed:



By analogy with the reaction with  $\text{PCl}_3$ , we may suppose two molecules of water to react, but the product  $\text{Cl}_3\text{P}(\text{OH})_2$ , if formed, at once loses water and gives  $\text{POCl}_3$ :



(ii) With *excess of water* the oxychloride forms phosphoric acid,  $\text{H}_3\text{PO}_4$ , which may be obtained directly from phosphorus pentachloride and a large amount of water:



Phosphorus pentachloride on heating sublimes, but the vapour density shows that it *dissociates*, the vapour consisting of

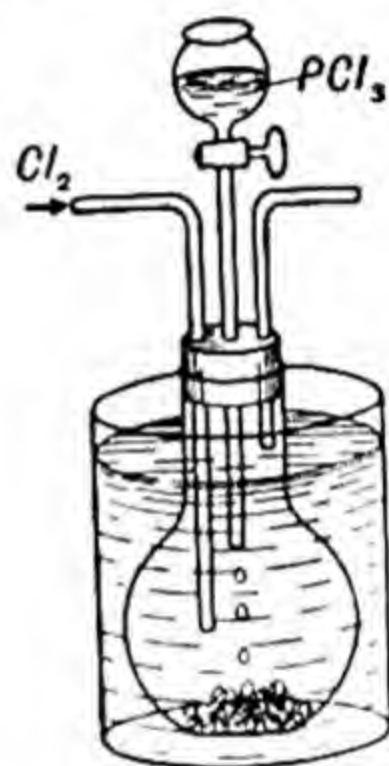
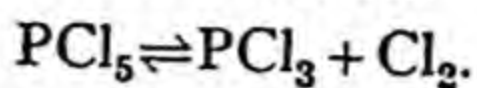


FIG. 310.—PREPARATION OF PHOSPHORUS PENTACHLORIDE BY THE ACTION OF CHLORINE ON THE TRICHLORIDE.

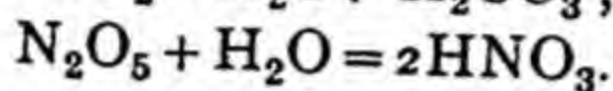
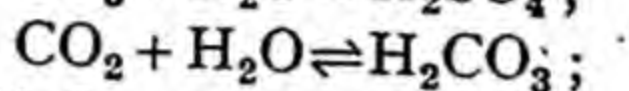
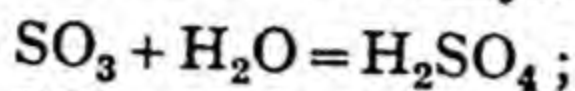
phosphorus trichloride and chlorine. These recombine on cooling :



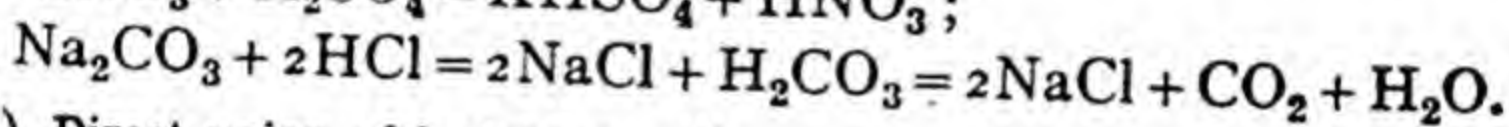
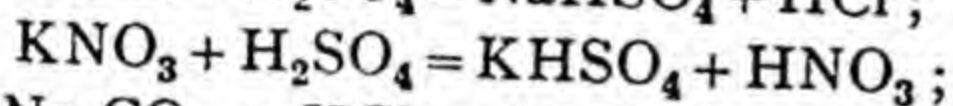
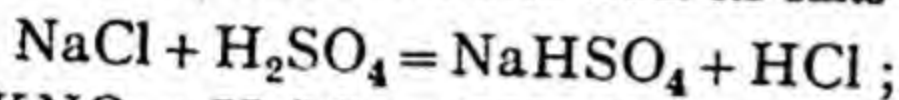
By adding excess of trichloride to the vapour, dissociation is prevented. This is an example of mass action (p. 222).

**Formation of acids.**—We may recapitulate the reactions leading to the formation of acids :

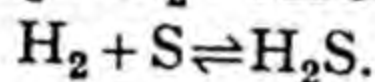
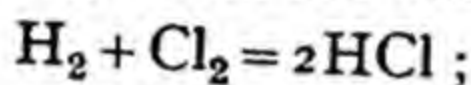
(1) Direct union of water and the acid anhydride :



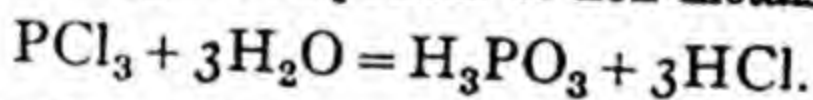
(2) Displacement of an acid from its salts by means of another acid :



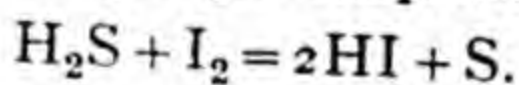
(3) Direct union of hydrogen with non-metals :



(4) Hydrolysis of halogen compounds of non-metals :



(5) Displacement from a hydrogen compound :



**Oxides of phosphorus.**—There are two important oxides of phosphorus :

phosphorus trioxide,  $\text{P}_2\text{O}_3$  or  $\text{P}_4\text{O}_6$  ;

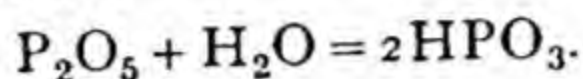
phosphorus pentoxide,  $\text{P}_2\text{O}_5$  or  $\text{P}_4\text{O}_{10}$ .

The first is formed by the combustion of phosphorus in a limited supply of air, the second by the combustion in a free supply of air.

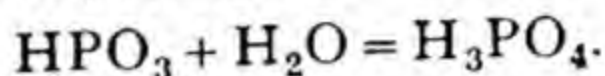
The air inside a bell-jar standing on a plate is dried by leaving a capsule of sulphuric acid under the jar. This is removed and replaced by a capsule containing a piece of dry white phosphorus the size of a pea, which is ignited by a hot wire and quickly covered with the jar. The phosphorus at first burns with a *bright white* flame, forming white clouds of phosphorus pentoxide which settle out like flakes of snow. After a time the flame becomes *pale greenish and non-luminous* : phosphorus trioxide is then formed.



Phosphorus pentoxide is a white powder which volatilises at a red heat. The vapour density corresponds with  $P_4O_{10}$ . It is very deliquescent, and on exposure to moist air rapidly deliquesces to a sticky mass of metaphosphoric acid,  $HPO_3$ . This is also formed when the pentoxide is thrown into cold water, when it hisses like red-hot iron, and flocks of metaphosphoric acid settle out :



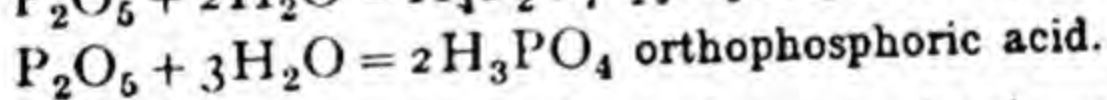
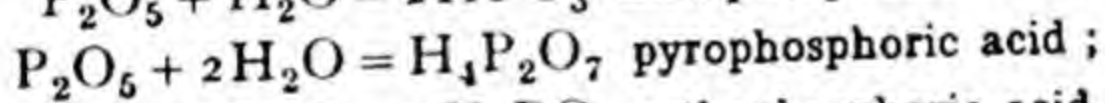
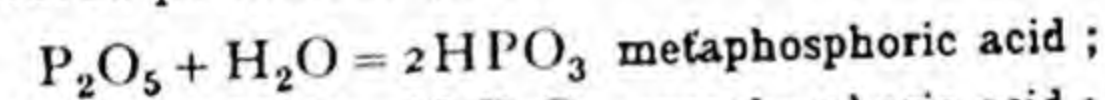
On boiling the solution, orthophosphoric acid,  $H_3PO_4$ , is formed :



Phosphorus pentoxide has a most intense attraction for water. It removes all traces of water vapour from gases, and will even 'remove the elements of water' from other substances, such as nitric acid (p. 391) and sulphuric acid (p. 355).

Phosphorus trioxide, which is not phosphorescent when pure, with ice-cold water forms phosphorous acid,  $H_3PO_3$  (cf. p. 465).

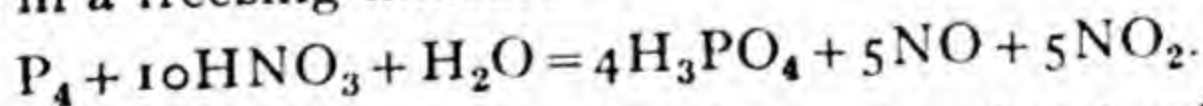
**The phosphoric acids.**—There are three phosphoric acids, all of which may be regarded as formed by the addition of water to phosphorus pentoxide (hence termed **phosphoric anhydride**) :



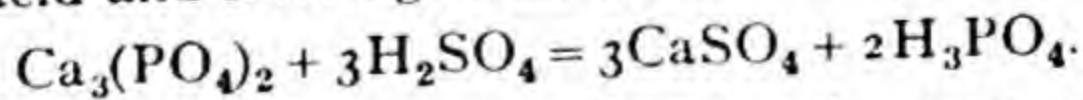
Common phosphoric acid is orthophosphoric acid,  $H_3PO_4$ . It may be obtained :

(1) By dissolving phosphorus pentoxide in water and boiling to convert the meta- into ortho-phosphoric acid.

(2) By boiling *red* phosphorus with nitric acid (white phosphorus is liable to explode), evaporating till the temperature rises to  $180^\circ$ , and crystallising by cooling in a vacuum desiccator standing in a freezing mixture :



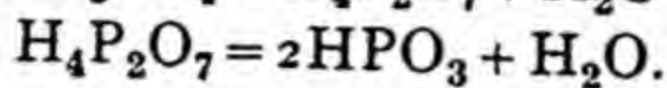
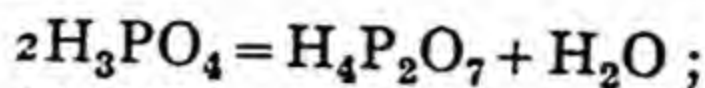
(3) By digesting bone ash (calcium phosphate) with dilute sulphuric acid and filtering from calcium sulphate :



(4) By heating a phosphate mineral, coke, iron and silica in the electric furnace in a current of air, and collecting the  $P_2O_5$  fumes in presence of moisture.

Phosphoric acid is usually sold in the form of solution, which

has no smell and a strong acid taste. Pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , is formed when orthophosphoric acid is heated for some time at  $230^\circ$ ; metaphosphoric acid ('glacial phosphoric acid') is formed as a glassy mass when ortho- or pyro-phosphoric acid is heated to redness:



**The phosphates.**—Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is *tribasic* and forms *three* series of salts, all of which are called simply 'phosphates':

primary phosphate: sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$ ;

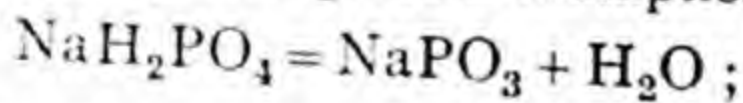
secondary phosphate: disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ ;

tertiary phosphate: trisodium phosphate,  $\text{Na}_3\text{PO}_4$ .

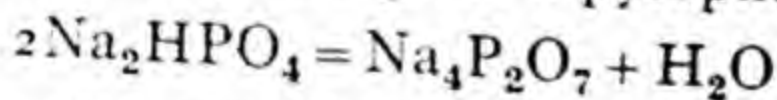
The secondary phosphate is ordinary 'sodium phosphate,'  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . It is made by neutralising caustic soda or sodium carbonate with phosphoric acid and crystallising. Although it is an 'acid salt' (p. 148) it is practically neutral, really faintly alkaline, in reaction. By adding another portion of phosphoric acid to the disodium salt the primary phosphate is obtained,  $\text{NaH}_2\text{PO}_4$ , acid in reaction. By crystallising the disodium salt from a solution containing *excess* of caustic soda, the tertiary phosphate,  $\text{Na}_3\text{PO}_4$ , with a strongly alkaline reaction owing to hydrolysis, is formed.

The action of heat on the orthophosphates is important:

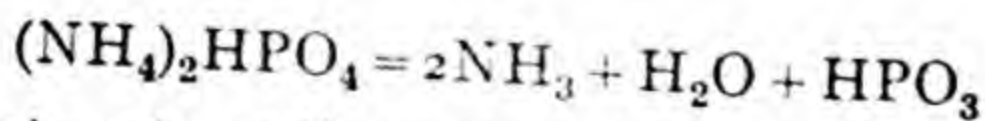
(1) the primary phosphate gives a metaphosphate:



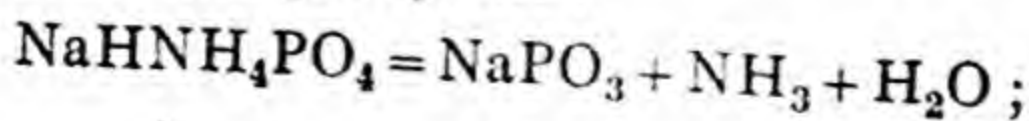
(2) the secondary phosphate gives a pyrophosphate:



except in the case of ammonium phosphate, which on heating evolves water and ammonia, and leaves a residue of metaphosphoric acid:



and *microcosmic salt*, sodium ammonium hydrogen phosphate, which on heating gives off ammonia and water and leaves a residue of sodium metaphosphate:

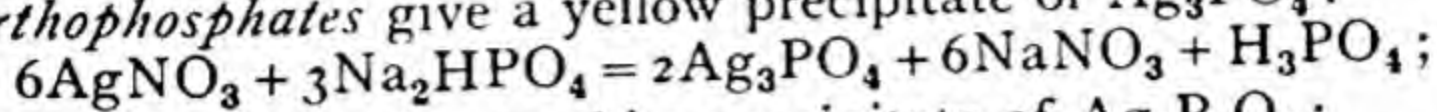




(3) the tertiary phosphate is unchanged.

The action of silver nitrate on phosphate solutions is important:

*orthophosphates* give a yellow precipitate of  $\text{Ag}_3\text{PO}_4$ :



*pyrophosphates* give a white precipitate of  $\text{Ag}_4\text{P}_2\text{O}_7$ ;

*metaphosphates* give a white gelatinous precipitate of  $\text{AgPO}_3$ .

Metaphosphoric acid alone coagulates albumin (white of egg). Orthophosphates give a *yellow* precipitate with ammonium molybdate on standing in the cold in presence of nitric acid, pyro- and meta-phosphates only on heating.

### SILICON.

**Silica.**—Next to oxygen, silicon is the most abundant element in the crust of the earth (p. 80): it occurs in combination with oxygen as *silicon dioxide*, or *silica*,  $\text{SiO}_2$ , varieties of which are quartz, sand, flint, etc. Silica is also the acidic constituent of the very abundant *silicate rocks*. Granite and similar primitive rocks contain from 20 to 30 per cent. of silicon. Rocks, stones, sand, glass, bricks, pottery, mortar, cement, and water-glass all consist of, or contain large quantities of, silica, so that the element silicon is clearly one of great importance in everyday life.

Silica, although insoluble in water, has an acidic character, as was pointed out by Otto Tachenius in 1666: it dissolves in potash, forming a solution of a silicate, formerly known as *liquor of flints*. Tachenius also observed that acids differ in strength; one acid is displaced from its compounds by a stronger acid. The acidic character of silica explains the formation of *slags* in metallurgical operations. These are glassy or stony masses formed in smelting ores containing silica or silicates, to which lime has been added, and consist principally of the silicates of calcium and aluminium.

Lavoisier, who included silica among the earths, expressed the opinion that the latter 'must soon cease to be considered as simple bodies,' and are probably 'compounds consisting of simple substances, perhaps metallic, oxydated to a certain degree.' Gay-Lussac and Thenard in 1811 obtained silicon, the element of which silica is the oxide. In most of its properties silicon belongs to the group of non-metallic elements, although it forms alloys with metals, such as copper and iron. It differs from carbon, which also forms alloys, by giving a solid, difficultly fusible dioxide,  $\text{SiO}_2$ .

**The forms of silica.**—Silica occurs both *crystallised* and *amorphous*. The main crystalline form is **quartz**. Two other crystalline forms of silica are known: **tridymite** and **cristobalite**.

Silica occurs not only in the mineral kingdom, but also as a constituent of vegetable and animal organisms. It is found in the straw of cereals and the bamboo cane, in the common weed 'horse-tail,' in the feathers of some birds, and in sponges. Vast deposits of almost pure silica are found in the form of *kieselguhr*, which consists of the siliceous skeletons of extinct diatoms.



FIG. 311. QUARTZ CRYSTALS.

This material, being very porous, is used to absorb nitroglycerin in the preparation of dynamite, and in lagging steam pipes to check loss of heat.

Dissolved silica occurs in the water of geysers and is deposited at the mouth of the geyser as *sinter*. It may also pass into the pores of wood, etc., in the earth, producing *petrification*.

**Quartz.**—Quartz, or *rock crystal*, occurs sometimes in clear, colourless crystals (Fig. 311) used for the preparation of spectacle lenses ('pebbles'), prisms, and optical apparatus, but more frequently in opaque or coloured masses. Coloured varieties of quartz (e.g., purple, in *amethysts*) are used as gems. *Sand* consists of quartz, which remains unchanged after the disintegration, or 'weathering,' of rocks, and has been crushed during its movement by water. The purest forms of sand are



white ('Calais sand'); yellow sand is coloured by ferric oxide. *Sandstone* consists of sand grains cemented together with oxide of iron, or other materials. 'Musical or Singing sand,' which emits a peculiar squeaking note when pressed, consists of rounded grains of nearly uniform size. It occurs in patches along with ordinary sand in various localities—e.g., near Poole.

**Amorphous silica.**—All varieties of silica fuse in the oxygen-hydrogen blowpipe. They become plastic before fusion, and may be worked and blown like glass, or drawn into thread. The amorphous, vitreous product, called *quartz glass*, has a very small coefficient of expansion, and may therefore be heated to redness and quenched in cold water without fracture. (Quartz crystals crack violently when heated to 500°-600°.) Quartz is transparent to the ultra-violet rays, whilst ordinary glass is largely opaque to them.

Large blocks of clear quartz can be made by joining separate pieces together by fusing them in a furnace and giving an alternate vacuum and pressure treatment to get rid of air bubbles. It has been successfully used for lenses in cinema lanterns since it does not crack on heating, and it may even be possible to prepare large sheets for hospital windows, in which case the valuable ultra-violet rays of the sun, which are largely cut out by ordinary glass, would be freely transmitted. Ultra-violet light when too powerful is injurious. **Crookes's glass**, which absorbs the ultra-violet rays which cause eye-strain, is glass containing compounds of 'rare earths.' Glass containing titanium oxide is also used for the same purpose. Ultra-violet rays are given off in electric arc welding and the eyes and skin of the workmen require suitable protection.

Besides transparent silica obtained by fusion, a translucent variety, known as *vitreosil*, is manufactured by fritting sand with an electrically-heated carbon rod or plate (Fig. 312).

Amorphous silica occurs in Nature in a variety of forms, some of which are combined with crystalline forms in gems such as *chalcedony*, *carnelian*, *chrysoprase* and *sard*.

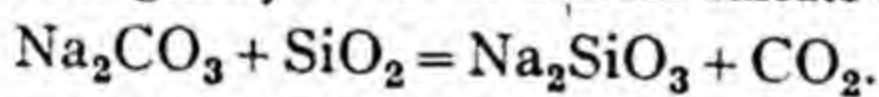
Common *flint* occurs in rounded nodules in chalk, coloured yellow, grey, or black by oxide of iron. It is very hard, and splits with a conchoidal fracture, giving sharp edges—hence its use in the 'Stone Age.' The *opal* contains combined water, and has, like other amorphous varieties, apparently been formed by the drying of colloidal silica (*q.v.*).

**Silicates.**—Silica,  $\text{SiO}_2$ , is an acidic oxide, and may be regarded as the anhydride of silicic acid,  $\text{SiO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SiO}_3$ , just as carbon dioxide is the anhydride of carbonic acid:  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ . Their salts, the carbonates and silicates, are very stable.



FIG. 312.—VITREOSIL APPARATUS.

When silica, *e.g.*, sand or powdered quartz, is fused with sodium carbonate a glassy mass of sodium silicate is formed:



This dissolves on boiling with water, and the thick concentrated solution is called **water-glass**. It is used in preserving eggs, which it does by stopping up the pores in the shell, for rendering concrete oil-proof and non-dusty, and, mixed with asbestos powder, in forming *uralite* boards for roofing, etc.

Acids decompose a solution of sodium silicate, throwing down a gelatinous mass of *hydrated* silica; when washed and dried this forms a hard glassy mass called **silica gel**, which has great adsorptive power (p. 409), probably because it contains a multitude of fine capillary pores. When gelatinous hydrated silica is heated it forms a white powder of amorphous silica.

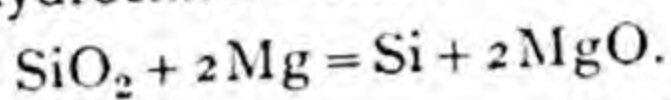
At high temperatures, silica, being a practically non-volatile acidic oxide, is able to displace volatile acids from their salts (p. 366). It is, however, relatively inert and refractory, and is used for making *refractory bricks* (ganister, Dinas brick, etc.) for furnace linings.

**Silicon.**—Silicon has a great affinity for oxygen, so that the direct reduction of silica by carbon occurs only at very high temperatures in the electric furnace:  $\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}$ . By heating a mixture of sand and coke in proper proportions in



the electric furnace the very hard **silicon carbide**, which is used as an abrasive, is formed:  $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$ . Silicon is a hard, grey, crystalline solid used in making certain alloys. *Silicon steel* is used for the cores of electromagnets in transformers: it is more magnetic than Swedish iron under low magnetising forces, and hysteresis losses are much reduced. Iron containing some carbon and more than 15 per cent. of silicon resists the action of nitric and sulphuric acids.

In the laboratory, amorphous silicon is obtained as a light brown powder by heating silica with magnesium powder, when a very violent action occurs, and dissolving out the magnesium oxide with dilute hydrochloric acid:



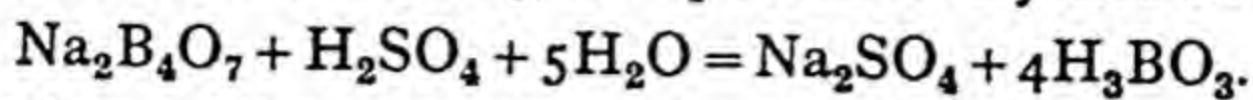
It burns in chlorine forming the volatile liquid tetrachloride,  $\text{SiCl}_4$ , which is also formed by passing chlorine over a strongly heated mixture of silica and carbon. By the action of acid on magnesium silicide a spontaneously inflammable gaseous **silicon hydride**,  $\text{SiH}_4$ , is formed.

**Colloidal silica.**—When an acid is added to a solution of sodium silicate, a gel of hydrated silica is precipitated, but if the dilute solution of the silicate is added to the acid, say hydrochloric acid, no precipitation of silica occurs. The liquid may then be supposed to contain sodium chloride and a colloidal solution, or *sol*, of silica. If it is poured into a dialyser, the sodium chloride diffuses away, and a clear sol of silica (or of 'silicic acid'), which does not diffuse through the membrane because it is colloidal, remains in the dialyser. This was discovered by Graham in 1861. The solution is coagulated by the addition of certain salts and the gel is formed.

Colloidal silica is a rather special and perhaps not very interesting case of a great number of solutions constantly met with in everyday life, called colloidal solutions (p. 176). Colloidal silica is not really so unimportant as might be thought, since a large number of important minerals and rocks have almost certainly been deposited in the course of ages from natural colloidal solutions of silica.

\* **Boron.**—The most important compounds of boron are boric (boracic) acid,  $\text{H}_3\text{BO}_3$ , and its sodium salt **borax**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . Boric acid is volatile in steam and occurs in some natural steam jets in Tuscany, from which it is extracted. Borax occurs in some lakes, and is also prepared by boiling calcium and magnesium borate minerals with sodium carbonate solution.

By adding hydrochloric acid or sulphuric acid to a hot solution of borax, boric acid,  $\text{H}_3\text{BO}_3$ , is deposited as crystals on cooling :



The acid is a mild antiseptic, and since it is a *very* weak acid it may be used in weak solution as an eye lotion. *Boracic ointment* contains the acid mixed with lard or vaseline. On heating, boric acid loses water and fuses to a glassy mass of its anhydride, boron trioxide,  $\text{B}_2\text{O}_3$ . When heated with potassium or magnesium this yields boron, a dark brown powder insoluble in water and most acids.

Borax is used as a *flux* in hard soldering, since in the fused state it dissolves oxides of many metals and leaves the metal surface clean. For ordinary soldering ('soft soldering') a solution of zinc chloride or sal-ammoniac, or resin, is generally used. Borax is used in the laundry for softening water, in making some kinds of glass, enamels, and glazes for pottery, and as an antiseptic. Many metallic oxides dissolve in a globule of fused borax on a platinum wire to yield masses with characteristic colours ; cobalt gives a deep blue 'borax bead.'

\* **Arsenic.**—Arsenic is an element which is chemically analogous to phosphorus. Like the latter, it exists in allotropic modifications, one of which resembles white phosphorus by oxidising in air at room temperature, and exhibiting phosphorescence. The common variety is a brittle solid with metallic lustre. Arsenic occurs very widely distributed, especially in some ores of metals, from which it is separated, by roasting, in the form of arsenious oxide,  $\text{As}_2\text{O}_3$ , the common *white arsenic* (or simply 'arsenic') of commerce. This is extremely poisonous and is used in preserving skins, etc., and dissolved in caustic soda in the form of sodium arsenite,  $\text{Na}_3\text{AsO}_3$ , as sheep-dip and weed-killer. Arsenious oxide is used in making glass and some pigments. Arsenic forms a gaseous hydride, arsine (or arseniuretted hydrogen),  $\text{AsH}_3$ , analogous to phosphine, which is formed when a compound containing arsenic is added to a mixture of zinc and dilute sulphuric acid evolving hydrogen. It is decomposed by passage through a heated glass tube, with deposition of a black mirror of arsenic (*Marsh's test*). Arsenic acid,  $\text{H}_3\text{AsO}_4$ , is obtained by oxidising arsenious oxide with concentrated nitric acid ; lead arsenate and calcium arsenate are used in spraying fruit trees to check parasites ; they are very poisonous.



# QUESTIONS

## PART II

### NON-METALLIC ELEMENTS

1. How would you prepare a specimen of oxygen gas? What experiments would you perform in order to demonstrate its principal properties? How would you prove experimentally (i) that oxygen is contained in the atmosphere, (ii) that only one-fifth of the atmosphere is oxygen?

2. Give a list of *four* methods by which oxygen may be obtained from the air. Describe, in some detail, *one* of these methods which has practical importance. Why is the percentage of oxygen in the atmosphere very nearly constant all over the world, in spite of its being used up in animal respiration, combustion, etc.? [London Gen. School.]

3. Describe the method you would employ and the precautions you would take to determine experimentally the percentage weight of oxygen contained in potassium chlorate. How would you show that the residue after getting rid of the oxygen (a) is a chloride, (b) contains potassium? [Joint Matric. Board School Cert.]

4. Describe briefly *three* methods of preparing oxygen. How would you remove from oxygen traces of (a) carbon dioxide, (b) water vapour? [Camb. Local Jun.]

5. How could you obtain oxygen gas from the atmosphere? [India, U.P.]

6. Describe simple experiments you have performed, or seen performed, naming the substances employed, to illustrate *four* only of the following:

- (a) The loss of water of crystallisation by a salt on heating.
- (b) The evolution of oxygen on heating a substance.
- (c) A metal burning in a gas.
- (d) Decrepitation.
- (e) Bleaching.
- (f) Sublimation.

In each case state carefully what would be observed during the experiment. [Joint Matric. Board School Cert.]

7. Describe the preparation and properties of ozone. On partly ozonising 250 c.c. of oxygen a decrease of volume of 12.5 c.c. resulted. If the resulting gas was treated with excess of potassium iodide, calculate what volume of gas would remain and what weight of iodine would be liberated. [London Matric.]

8. Write an account of the preparation, properties and probable constitution of ozone. Give three characteristic tests for this substance. [Central Welsh Board, Higher.]

9. How is ozone prepared, and what are its principal properties? Describe and explain its action on (i) potassium iodide, (ii) hydrogen peroxide, (iii) lead sulphide.

10. Describe the preparation of hydrogen on a large scale. Three gm. of water are treated as follows: (a) passed in the form of steam over red-hot magnesium, (b) acted upon by sodium. What volume of gas (calculated at N.T.P.) is produced in each case? [Camb. School Cert.]

11. A balloon of 1000 litres capacity is to be filled with hydrogen at  $27^{\circ}$  and 750 mm. What is the *minimum* quantity of iron required to liberate the necessary amount of hydrogen? [Calcutta Inter.]

12. Sketch the apparatus you have used to prepare and collect a jar of hydrogen by the action of dilute sulphuric acid on zinc. Suggest an alternative method of preparing hydrogen and write equations for both methods of preparation. How would you show (a) that water is formed when hydrogen is burnt in air, and (b) that hydrogen is a reducing agent? [Joint Matric. Board.]

13. Give a brief account of the action, if any, of steam on the following substances when heated: carbon, magnesium, iron, copper. [Camb. Local Sen.]

14. Describe carefully, and with full experimental detail, an experiment by which you could determine the amount of dissolved salts present in a given volume of sea-water. How would you show that the principal substance dissolved in sea-water is sodium chloride? [Univ. of Lond. Matric.]

15. State clearly your reasons for believing that the oxygen of the atmosphere is present in the free state and not in the combined form. [Central Welsh Board, Elementary.]

16. Describe an experiment which you have performed or seen performed for determining the percentage of oxygen in air. [Central Welsh Board, Elementary.]

17. Describe methods (one each) for the preparation of hydrogen from (a) cold water, (b) steam, (c) a dilute acid. What impurities, if any, are likely to be present in the gas prepared by each of these methods, and how would you propose to remove them?

Name *three* elements with which hydrogen can enter into direct union, stating the conditions under which union takes place in each case. [Central Welsh Board, Elementary.]



18. Describe three distinctly different methods of preparing hydrogen. [Civil Service, N. Ireland.]

19. What is meant by *hard* and *soft* water? What are the causes of the differences between a hard and a soft water? [Camb. Local Jun.]

20. What is the 'fur' usually found on the inside of a kettle in which ordinary tap water has been frequently boiled? Explain carefully how it has been formed and say how you would prove, experimentally, it to be the substance you say it is. [London Matric.]

21. A natural water is found to give a precipitate (a) on boiling, (b) on the addition of silver nitrate, (c) on the addition of a solution of barium chloride. In each case state the inference you would draw. [Madras S.L.]

22. When is a sample of water said to be *hard*? State how you would remove the different kinds of hardness, giving reasons for employing any particular process for the purpose. [Calcutta Inter.]

23. To what is the hardness of water due, and how may it be removed? 200 c.c. of water require 9 c.c. of  $N/50 \text{ H}_2\text{SO}_4$  for neutralisation with methyl orange. What weight of quicklime must be added, in the form of lime water, to soften 150 gallons of this water? [Allahabad Inter.]

24. Give some account of the properties of water in the liquid, solid, and gaseous states respectively, and compare them with the properties of other solids, liquids, and gases with which you are acquainted. [Camb. Local Sen.]

25. Describe the preparation of hydrogen peroxide. What is the action of this compound on (a) lead sulphide, (b) acidified potassium iodide, (c) silver oxide? [Oxford and Camb. School Cert.]

26. Under what circumstances do (a) carbon, (b) sodium, (c) magnesium, and (d) iron, react with water? State the products that are formed in each case, giving equations. [Calcutta Inter.]

27. Write a succinct account of the chief chemical and physical properties of water. Explain the differences in the behaviour of rain water, spring water, and sea water towards soap solution. [Central Welsh Board, Elementary.]

28. Make a list of all the metals which displace hydrogen from water, stating in each case the compound produced and the experimental conditions best suited for its formation. Which of these compounds are reduced back to the metal by the action of hydrogen, and under what conditions? What is the action of steam on red-hot charcoal? [Entrance Exam. Mysore Univ.]

29. How are chlorine monoxide and chlorine dioxide respectively prepared? What is the effect of heat on each and how does each react with aqueous potash? [Central Welsh Board, Higher.]

30. How would you prepare a pure dry specimen of chlorine from potassium chloride? Describe and explain the reactions which occur when chlorine is made to act upon (a) sodium hydroxide, (b) ammonia, (c) slaked lime.

31. Given a supply of common salt, manganese dioxide, concentrated sulphuric acid and the ordinary laboratory apparatus, state what gases you would be able to prepare and give equations for the reactions involved. In *two* cases describe fully how you would prepare and collect the gas in a pure, dry condition. [London Gen. School.]

32. Describe exactly, giving a diagram, how you would prepare and collect chlorine. Detail its main properties, emphasising those which make it of importance commercially. What happens when it is passed into (1) potassium bromide solution, (2) hot caustic potash solution, and (3) calcium hydroxide? [Educ. Institute of Scotland, Preliminary.]

33. Chlorine was formerly called oxymuriatic acid. Why was this? What reasons have you for saying that the early ideas as to the nature of chlorine are incorrect? [Madras Inter.]

34. Describe fully how you would obtain from sea water: (a) pure water, (b) a fairly pure specimen of sodium chloride. [Camb. Local Jun.]

35. How is hydrochloric acid prepared? Describe what happens when (a) dilute, (b) concentrated hydrochloric acid is distilled. [Camb. School Cert.]

36. Describe the preparation and collection of dry hydrogen chloride. Compare and contrast the behaviour of hydrogen chloride with that of chlorine towards (a) ammonia, (b) water, (c) potassium hydroxide. [London Matric.]

37. Devise an experiment to illustrate each of the following: (a) The change of colour when a chemical action takes place. (b) The formation of a solid when two gases are mixed. (c) The evolution of heat when two cold liquids are mixed. (d) The promotion of a chemical change by means of light. [India, U.P.]

38. How may pure oxygen and pure chlorine be prepared from potassium chlorate? Compare the properties of these two gases, and give as many examples as you can of the oxidising action of chlorine. [Central Welsh Board, Elementary.]

39. What is an oxidising agent? Illustrate your answer by reference to bleaching powder. How is bleaching powder prepared and what are its uses? [Queen's Univ. Belfast, Matric.]

40. Describe how hydrogen chloride gas is usually prepared, and state how you would obtain a small quantity of a saturated solution of this substance. Give some account of the chief properties of the solution. [Central Welsh Board, Elementary.]

41. State in a tabular form the similarities between chlorine, bromine, and iodine which have led to these elements being classed under one group, and show how the properties of the individual elements vary in a regular manner with their atomic weights.

(Cl = 35.5; Br = 80; I = 127.)

[Madras S.L.]



42. What are the principal properties of bromine? Outline methods for preparing any *two* compounds of bromine from the element.

43. Name the reagents that are used in the laboratory to prepare hydrobromic acid. Compare the action of concentrated sulphuric acid on sodium chloride and sodium bromide respectively. What do these chemical facts show concerning the relative reducing powers of hydrochloric and hydrobromic acids? [Dacca Inter.]

44. State and explain the changes that take place when (1) chlorine is passed through a solution of caustic potash, (2) water is poured on a mixture of potassium acid sulphate and washing soda, and (3) strong sulphuric acid is added to solid potassium iodide and gently warmed. [Madras S.L.]

45. How is iodine usually obtained? State its properties and uses. [Calcutta Inter.]

46. Describe in detail how you would prepare specimens of three different forms of sulphur. [Camb. Local Jun.]

47. Explain, with a diagram, the construction and mode of working of Kipp's apparatus for generating gases. With what materials would you charge the apparatus for preparing (a) carbon dioxide, (b) hydrogen, (c) hydrogen sulphide? Give the equations of the reactions which take place in each case. [London Matric.]

48. How would you prepare and collect hydrogen sulphide, using ferrous sulphide? Sketch the apparatus you would employ. What is the action of hydrogen sulphide upon: (a) sulphur dioxide, (b) aqueous solution of caustic soda, (c) aqueous solution of lead nitrate? [Joint Matric. Board School Cert.]

49. Describe an experiment to prove that hydrogen sulphide gas contains its own volume of hydrogen. State and explain the action that takes place when sulphur dioxide is passed through aqueous solutions of (1) hydrogen sulphide gas, (2) chlorine, and (3) caustic soda. Describe with examples three general methods of preparing sulphides. [Madras S.L.]

50. Draw a neat sketch of the Kipp's apparatus. Explain the manner in which you would fit up and use it to generate hydrogen sulphide. State clearly the function and mode of action of the different parts of the apparatus. [Madras S.L.]

51. What are the chief uses of hydrogen gas? Indicate two methods by which it is prepared on a large scale. Give the names and formulae, together with the usual method of preparation, of the compounds of hydrogen with each of the elements chlorine, nitrogen, and sulphur. Write your answer in tabular form. [London Gen. School.]

52. Describe fully the phenomena of allotropy as exhibited in the case of sulphur. [Queen's Univ. Belfast, Entrance Schol.]

53. An excess of ferrous sulphide was added to 80 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 650 c.c. at  $0^{\circ}\text{C}$ . and 760 mm. Calculate the normality of the acid.

54. How is hydrogen sulphide prepared in the laboratory? Describe the experiments you would perform to show that hydrogen sulphide is both an acid and a reducing agent. What reactions take place when the gas is passed through aqueous solutions of (a) caustic soda, (b) chlorine, (c) copper sulphate, (d) nitric acid?

55. How may it be shown that hydrogen sulphide is a compound of hydrogen and sulphur, and that it contains its own volume of hydrogen?

56. Give an explanation of the terms oxidation and reduction. Classify the following substances as oxidising and reducing agents and give examples of their behaviour: sulphur dioxide, chlorine, nitric acid, hydrogen sulphide. Give examples of the behaviour of any one substance you know can behave both as an oxidising agent and as a reducing agent. [London Matric.]

57. Describe and *explain* as far as you are able the appearance presented when copper turnings and concentrated sulphuric acid are heated together in a flask. Sketch the apparatus required for preparing and collecting the gaseous product of this reaction, and write the equation for the reaction. Make a list of the properties of the gas, and state how it will react with (a) sulphuretted hydrogen, (b) nitric acid, (c) water, (d) lead dioxide. [London Gen. School.]

58. How may sulphur dioxide be prepared? Describe experiments to illustrate the reducing properties of sulphur dioxide. [Camb. Local Jun.]

59. How would you prove that sulphur dioxide contains its own volume of oxygen? Give a neat sketch of the apparatus. [Calcutta Inter.]

60. Describe, giving equations, the action of dilute sulphuric acid on zinc, bleaching powder, and sodium carbonate, and of strong sulphuric acid on charcoal, copper, common salt, and saltpetre. [Camb. Local Sen.]

61. How may the combination of sulphur dioxide and oxygen be brought about on a commercial scale? How would you prepare from sulphuric acid *either* sulphur *or* oxygen?

62. You are given a mixture of sand and sulphur. Describe *two* totally different methods by which you could extract the sulphur. Starting from pure roll sulphur, how would you prepare a dilute solution of sulphuric acid? How would you prove sulphuric acid to be contained in your solution? [London Matric.]

63. How is sulphur dioxide prepared (a) in the laboratory, (b) on the large scale? What reactions take place when the gas is led into (a) chlorine water, (b) potassium hydroxide solution, (c) a mixture of nitrogen peroxide and water vapour? [Oxford and Camb. School Cert.]

64. A sample of sulphuric acid having a specific gravity of 1.51 contains 60.65 per cent. of pure sulphuric acid by weight. What volume of this acid would be required to furnish one litre of normal sulphuric acid? What experiments would you make in order to verify your calculation? [Camb. School Cert.]



65. Say what you understand by 'catalysis,' and give examples of substances which act catalytically.  
Discuss the contact process for the manufacture of sulphuric acid.  
[Central Welsh Board, Higher.]

66. Write a succinct account of the chemistry of the lead-chamber process for the manufacture of sulphuric acid. What is the effect of heating the following substances severally with sulphuric acid: copper, charcoal, oxalic acid?  
[Central Welsh Board, Higher.]

67. How is sodium thiosulphate usually prepared? State and explain what happens when an aqueous solution of this salt is added to (a) dilute sulphuric acid, (b) a solution of iodine in aqueous potassium iodide. What use is made of this latter reaction in the laboratory?  
[Central Welsh Board, Higher.]

68. The problem of how to make use on a large scale of atmospheric nitrogen has received considerable attention from chemists during the present century. State clearly some of the reasons for this and, without going into technical details, give a short account of any one manufacturing process devised with a view to the utilisation of this nitrogen.  
[London Gen. School.]

69. Describe a good laboratory method of preparing ammonia gas. Name four common desiccating agents. State which can and which cannot be used to dry ammonia and explain why. What two gases does ammonia contain and how can they be obtained separately from ammonia?  
[Madras S.I.]

70. What is the action of ammonia gas on (a) hydrochloric acid gas, (b) water, (c) chlorine, (d) heated sodium, (e) oxygen, when mixed and ignited? With what uses of ammonia are you acquainted?  
[London Gen. Elem. Sci.]

71. It is required to prepare dry ammonia gas and then pass it over heated copper oxide (CuO). Sketch the apparatus you would employ, and write equations for the reactions which take place. Explain how this experiment gives information as to what chemical elements are present in ammonia gas.  
[London Gen. School.]

72. How is nitric acid prepared in the laboratory? Starting from nitric acid, show how you would prepare (a)  $N_2O$ , (b)  $NO$ , (c)  $NO_2$ .  
[Calcutta Inter.]

73. Starting with nitric acid, how would you obtain nitrous oxide, nitric oxide, and nitrogen peroxide, each in the pure state?  
[Dacca Inter.]

74. Describe the preparation of nitric acid. How may the nitrogen in nitric acid be converted into (a) nitric oxide, (b) ammonia, (c) nitrous oxide?  
[Camb. School Cert.]

75. Being given a supply of sodium nitrate, and such other laboratory materials as may be necessary, explain fully how you would obtain pure specimens of nitrous oxide and nitric oxide gases respectively. What is the effect of strongly heating sodium nitrate (a) alone, (b) with charcoal?  
[London Gen. School.]

76. Describe the preparation of nitrous oxide. Write an account of its chemical and physical properties. [Camb. Local Jun.]

77. Find the composition of nitrous oxide from the following data (the volumes are reduced to N.T.P.): volume of gas taken = 10 c.c.; volume after addition of hydrogen = 28 c.c.; volume after explosion = 18 c.c.; volume after addition of oxygen = 27 c.c.; volume after second explosion = 15 c.c. [Calcutta Inter.]

78. If you were provided with an aqueous solution of ammonia and some concentrated nitric acid, how would you prepare and collect, from these materials, a *dry* specimen of nitrous oxide? Describe a method for determining the volume of nitrogen which can be obtained by decomposing a known volume of nitrous oxide.

[Camb. School Cert.]

[Note.—No materials, other than those provided, are to be used in drying the gas.]

79. You are provided with an aqueous solution of ammonia and concentrated nitric acid. Say exactly how you would prepare from these, and collect, a pure dry specimen of nitrous oxide. Explain briefly how you would show that nitrous oxide contains its own volume of nitrogen. [London Matric.]

80. What is *observed* when nitric acid, diluted with its own volume of water, is poured upon copper turnings? Sketch the apparatus required to collect the gaseous product, and write equations representing: (a) the formation of any intermediate products, (b) the complete reaction. Name the gaseous product; briefly describe how you would identify it, and demonstrate the presence of the elements in it.

[London Gen. School.]

81. Describe the action of heat on the following substances giving equations in each case: (a) ammonium chloride, (b) sodium nitrate, (c) calcium carbonate, (d) cupric nitrate and (e) ammonium nitrite.

[Calcutta Inter.]

82. How would you prepare nitrogen peroxide? Describe its physical and chemical properties. [Camb. Local Jun.]

83. How would you obtain (a) chlorine from hydrochloric acid and vice versa; (b) nitrogen from ammonia and vice versa; (c) sulphur from sulphuretted hydrogen and vice versa? [Calcutta Inter.]

84. Compare the modes of formation and properties (both physical and chemical) of the hydrides of nitrogen and sulphur. [Dacca Inter.]

85. (a) How would you prepare nitric oxide in the laboratory?  
(b) Explain what will happen if this gas is passed for some time slowly into a jar of air confined over water. [Civil Service, N. Ireland.]

86. What is the effect of heat on nitrates of the metals? Illustrate your answer by reference to the nitrates of potassium, ammonium, and lead respectively. Give one test by which you could distinguish a nitrate.

[Central Welsh Board, Elementary.]



87. Explain the method and make a sketch of the apparatus you would employ for the preparation of liquid nitrogen dioxide. Describe the appearance of the product and explain the reaction which occurs when it is added to water. The gas produced by warming the liquid nitrogen dioxide is gradually heated more and more strongly and then cooled gradually to the temperature of the laboratory. Describe and explain all that is observed to happen. [Univ. of Lond. Matric.]

88. How is charcoal manufactured? Describe the chief properties and uses of both charcoal and graphite, and contrast the properties of these substances with those of the diamond.

89. State briefly the chief differences between elements, mixtures, and compounds. Refer to the chemical nature of the following substances in illustration of your answer: air, water, iodine, silica, sodium, glass. Name some of the more important naturally occurring substances in which *carbon* is present (a) as an element, (b) in chemical compounds. [London Gen. School.]

[Note.—Air and glass are not 'mixtures' in the correct sense: they are solutions.]

90. How would you show that graphite is an allotropic form of carbon? Mention one other element which occurs in allotropic forms and describe the preparation and appearance of each form. [Oxford and Camb. School Cert.]

91. Give a full account of the allotropic forms of carbon. [Allahabad Inter.]

92. Describe the preparation and properties of a *pure* and *dry* specimen of carbon monoxide. If you were given a mixture of carbon monoxide and hydrogen, how would you estimate the quantities of each present? [Camb. School Cert.]

93. What volume of air at  $27^{\circ}$  and 750 mm. would be required for the complete combustion of a gaseous mixture containing 46 per cent. hydrogen, 40 per cent. marsh gas and 14 per cent. carbon monoxide by volume. Air contains 79 per cent. nitrogen and 21 per cent. oxygen by volume. [Calcutta Inter.]

94. Assuming air to contain 21 per cent. by volume of oxygen, what volume of air at  $27^{\circ}$  and 755 mm. will be required for the complete combustion of one litre of each of the following gases at the same temperature and pressure: (a) hydrogen, (b) methane, (c) carbon monoxide? [Calcutta Inter.]

95. Describe a method of determining the density of carbon monoxide. 5.5 c.c. of concentrated formic acid (sp. gr. 1.22) were diluted to 100 c.c. and 7.6 c.c. of the diluted acid required for neutralisation 10 c.c. of *N* NaOH. Calculate the weight of undiluted acid required to yield 250 c.c. of carbon monoxide. [Madras Inter.]

96. The gas obtained by the action of sulphuric acid on oxalic acid was rapidly passed through a dilute solution of caustic soda and then suitably dried. It was analysed in a eudiometer as follows :

Vol. of gas taken, 12.6 c.c. ; vol. after addition of oxygen, 21.1 c.c. ; vol. after explosion, 14.9 c.c. ; vol. after absorption with caustic potash, 2.3 c.c. (all at the same temp. and press.). What do you conclude as to the nature of the gas analysed ? [Madras Inter.]

97. What reasons have you for supposing that there is twice as much oxygen in a given volume of carbon dioxide as in an equal volume of carbon monoxide ? How would you attempt to compare the solubilities of these two gases in water ? [Madras Inter.]

98. How and under what conditions do hydrogen and carbon monoxide react upon (a) copper oxide, (b) chlorine ? Suggest a method by which *one* of the constituents could be separated from a mixture of hydrogen and carbon monoxide. How would you show whether it had been obtained in a pure condition ? [London Gen. School.]

99. Describe a method and sketch the apparatus required for preparing and collecting pure *dry* carbon dioxide gas. How can this gas be converted into carbon monoxide ? 10 c.c. of carbon monoxide are exploded with 20 c.c. of oxygen in a eudiometer, over mercury. What volume of gas is left, and what is its composition ? (All volumes are measured at the same temperature and pressure.)

[London Gen. School.]

100. What experiments would you make in order to ascertain whether carbon when oxidised completely reacts with oxygen according to the equation  $C + O_2 = CO_2$  ? [Camb. School Cert.]

101. Two volumes of a certain gas when exploded with five volumes of oxygen yield exactly four volumes of carbon dioxide and two volumes of steam. One hundred and four grams of the gas occupy the same volume as a hundred and seventy-six grams of carbon dioxide, measured under the same conditions. What is the gas, and how would you prepare a crude sample of it ? ( $H=1$  ;  $O=16$  ;  $C=12$ .)

[Queen's Univ. Belfast, Entrance Schol.]

102. What amount of marble will have to be dissolved in hydrochloric acid in order to produce 15 litres of carbon dioxide at  $27^\circ$  and 750 mm. ? What weight of pure carbon will give that amount of carbon dioxide on combustion ? [Calcutta Inter.]

103. Write a short account of the discovery of carbon dioxide. What name did its discoverer give to it, and why ? What properties of the gas did he discover, and how ? Give as many methods as you can for its preparation. [Madras S.L.]

104. Write notes on the practical uses of the following substances : ammonia, chlorine, carbonic acid gas, and water. [India, U.P.]

105. Give a full account of the successive changes you see when carbon dioxide is passed into lime water. How do you explain these changes ? [India, U.P.]



106. When sugar is completely burnt in the air certain gases are produced. Describe fully how you would show that these gases are also contained in the breath exhaled by human beings. Explain the use of plants in purifying air. What is the function of nitrogen in the atmosphere? [India, U.P.]

107. Give a list of the chief drying agents used for (a) gases, (b) liquids. Stating your reasons, name the drying agents you would use for each of the following gases: sulphur dioxide, sulphuretted hydrogen, carbon monoxide, ammonia, hydrochloric acid gas, carbon dioxide. Define the terms *deliquescent* and *efflorescent*, naming, with their formulae, two examples in each case. [London Gen. School.]

108. Describe what happens when carbon dioxide is passed through a solution of potassium hydroxide, and compare the action with that of the same gas on lime water. [Central Welsh Board, Elementary.]

109. How can it be shown that the gas obtained by heating marble is the same as that obtained by treating marble with hydrochloric acid? Give three tests (one, quantitative). Write an account of the part played by this gas in Nature. [School Leaving Certificate (Higher), Scotland.]

110. Four bottles are given to you containing oxygen, hydrogen, nitrogen, and carbon dioxide. By what experiments would you distinguish these gases from one another? [India, U.P.]

111. One and a half grams of a sample of coal containing 85 per cent. carbon, 5 per cent. hydrogen, and 10 per cent. oxygen are completely burnt in a current of dry air free from carbon dioxide, and the products passed successively through two weighed U-tubes filled respectively with calcium chloride and soda-lime. Calculate the alterations if any in the weights of the tubes. [Calcutta Inter.]

112. Sketch and describe the use of apparatus by means of which you could demonstrate the presence of the two chief products of combustion obtained when coal gas burns in air. Give an account of an experiment which shows that coal gas acts as a *reducing agent*. Name two other reducing agents, giving examples of their use. [London Gen. School.]

113. Mention the different forms of carbon which occur naturally. Describe the manufacture by means of the electric furnace of any two of the following substances: graphite, carborundum, calcium carbide. [Queen's Univ. Belfast, Matric.]

114. Explain the difference between carbonates and bicarbonates, illustrating your answer by reference to the corresponding salts of another acid. [School Leaving Certificate (Higher), Scotland.]

115. State the law of combination of gases by volume. 5 c.c. of ethylene are mixed with 20 c.c. of oxygen and sparked. What is the composition by volume of the products of the reaction, all measurements being made at a temperature above  $100^{\circ}\text{C}$ . [Camb. School Cert.]

116. Twenty-five c.c. of marsh gas at N.T.P. are mixed with 300 c.c. of air at  $27^{\circ}\text{C}$ . and 750 mm. pressure, and the mixture is exploded by electric sparks. Find the volume of the residual gas at  $17^{\circ}\text{C}$ . and 750 mm. Air contains 20 per cent. of oxygen and 80 per cent. of nitrogen by volume. [Calcutta Inter.]

117. Ten c.c. of a gaseous hydrocarbon are exploded with 25 c.c. of oxygen. The mixture contracts to 15 c.c. On adding potash a further contraction of 10 c.c. takes place and the residue is found to be pure oxygen. What is the molecular formula of the hydrocarbon if its density be 8? [Calcutta Inter.]

118. Compare the properties of ethylene with those of methane. What volume of oxygen would be required for the complete combustion of 250 c.c. of each of these gases? [Camb. Local Sen.]

119. Enunciate Avogadro's hypothesis. 25 c.c. of ethylene at  $100^{\circ}\text{C}$ . and 760 mm. are exploded with 150 c.c. of oxygen. State the volume and composition of the residual gas under the same conditions of temperature and pressure. What would be the result if instead of ethylene (a) 25 c.c. of carbon monoxide, (b) 25 c.c. of methane, were treated similarly? [London Matric.]

120. How is methane usually prepared and collected? State its principal properties and explain carefully what happens when it is (a) led over red-hot cupric oxide, (b) burnt in an atmosphere of chlorine. [London Matric.]

121. How would you distinguish between methane and a mixture of ethylene with twice its volume of hydrogen? What volume of oxygen is necessary to burn completely one litre of ethylene, both volumes being measured at the same temperature and pressure? [London Matric.]

122. What reagents would you employ to remove small quantities of (a) carbon dioxide from carbon monoxide, (b) sulphur dioxide from ethylene, (c) nitric oxide from nitrous oxide, (d) hydrogen sulphide from hydrogen, (e) chlorine from oxygen? Give reasons for your selection. [Camb. School Cert.]

123. What is a flame? Explain fully the structure of a candle flame, describing simple experiments in support of your explanation. Is there any difference between a candle flame and that of a Bunsen burner? If so, explain the nature and cause of the difference. [Calcutta Inter.]

124. State what chemical changes occur when a candle is burnt in air, and describe experiments in support of your answer. Give an account of the structure of a candle flame. [London Gen. School.]

125. Describe Davy's safety lamp and explain fully its action. State the circumstances under which its usefulness is impaired. [Calcutta Inter.]

126. Assuming that air contains 23 per cent. by *weight* of oxygen, find the *volume* of air at  $27^{\circ}\text{C}$ . and 750 mm. pressure that would be required for the complete combustion of one kilogram of coal containing 90 per cent. of carbon and 5 per cent. of hydrogen. [Calcutta Inter.]



127. What do you understand by combustion? How far are the terms *combustible substance* and *supporter of combustion* applicable to one and the same substance? Describe experiments to illustrate your answer. [Camb. School Cert.]

128. How are yellow and red phosphorus obtained from calcium phosphate? Compare the chemical and physical properties of these substances and describe some experiments to prove that both are forms of the same element. [Oxford and Camb. School Cert.]

129. Describe experiments to demonstrate the differences in the properties of the common forms of phosphorus. How would you show that they are varieties of one and the same element. [Madras S.I.]

130. Compare the methods of preparation and chemical properties of sulphuretted hydrogen, ammonia, and phosphine. What other well-known compounds suggest that nitrogen and phosphorus belong to the same group of elements? [Madras Inter.]

131. Seven unlabelled bottles contain respectively one of the following solid substances: (a) anhydrous sodium carbonate, (b) sodium bicarbonate, (c) potassium iodide, (d) potassium bromide, (e) sodium sulphite, (f) ammonium nitrite, (g) phosphorus pentoxide. Describe simple tests by means of which you could identify the substances. Arrange your answer in *tabular form*. [London Gen. School.]

132. (a) Describe fully the physical and chemical properties of silica. State if it is acidic or basic. (b) In what forms does silica occur in Nature? [Allahabad Inter.]

133. What experiments would you make with (a) charcoal, (b) silica, (c) quicklime to show the general chemical behaviour of these substances? [London Matric.]

134. What is the chemical formula of silica? Adduce evidence in support of the statement that silica is an 'acid-forming oxide.' How would you prepare an aqueous solution of the acid? [London Matric.]

135. With what classes of oxides are you acquainted, and how can you distinguish between them? Illustrate your answer with reference to the following: lime, silica, black oxide of manganese, carbon monoxide, and carbon dioxide. Explain briefly, with examples, the meaning of the terms anhydride and alkali respectively. [London Gen. School.]

136. Write a note on the occurrence, properties, and uses of silica. [Queen's Univ. Belfast, Matric.]

137. Say briefly how the following are prepared from ordinary white sand: (a) silicon, (b) soluble silicic acid, (c) silicon chloride. Describe the principal properties of any *one* of them. [Central Welsh Board, Higher.]

138. Describe the preparation and properties of the two chlorides of phosphorus. What happens when they are treated with water? [Central Welsh Board, Higher.]

## ANSWERS TO QUESTIONS

7. 212.5 c.c. ; 0.2858 gm.      11. 753.7 gm.      23. 17.175 gm.  
53. 0.73 N.      64. 53.6 c.c.      93. 5833 c.c.  
94. (a) 2.38 litres ; (b) 9.52 litres ; (c) 2.38 litres.      95. 5.70 gm.  
96. 12.4 c.c. CO ; 0.2 c.c. CO<sub>2</sub>.  
99. 25 c.c. ; 10 c.c. CO<sub>2</sub>, 15 c.c. O<sub>2</sub>.  
101. Acetylene, C<sub>2</sub>H<sub>2</sub>.      102. 60.2 gm. ; 7.2 gm.  
111. 0.0083 gm. ; 4.675 gm.  
115. 42.5% CO<sub>2</sub> ; 42.5% H<sub>2</sub>O (steam) ; 5% O<sub>2</sub>.  
116. 268 c.c.      117. CH<sub>4</sub>.      118. 750 c.c. ; 500 c.c.  
119. 175 c.c. ; 75 c.c. O<sub>2</sub>, 50 c.c. CO<sub>2</sub>, 50 c.c. H<sub>2</sub>O (steam).  
    (a) 163.5 c.c. ; 138.5 c.c. O<sub>2</sub> ; 25 c.c. CO<sub>2</sub>.  
    (b) 175 c.c. ; 100 c.c. O<sub>2</sub>, 25 c.c. CO<sub>2</sub>, 50 c.c. H<sub>2</sub>O (steam).  
126. 980.6 litres.



*PART III*  
ORGANIC CHEMISTRY AND METALS





## CHAPTER XXVII

### ORGANIC COMPOUNDS

**Organic compounds.**—Compounds of carbon containing either hydrogen or oxygen combined with carbon have been considered in Chapter XXV. In the present chapter some important substances containing *carbon combined with both hydrogen and oxygen* will be described. These include carbohydrates (such as starch, sugar, and cotton), alcohol, and organic acids, together with the substances derived from them, such as soap, explosives, and dyes. Some hydrocarbons not previously described, such as those prepared from coal tar (benzene, toluene, naphthalene, anthracene), rubber, and essential oils (perfumes, turpentine, etc.) are included. The importance of all these materials in everyday life is evident, but they are usually omitted from elementary courses in chemistry.

**Carbohydrates.**—The name carbohydrate is usually given to a group of important compounds containing carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen is the same as in water (*cf.* p. 403). They are present in important foods, in many fabrics or textiles (such as cotton and linen), in paper, and in starch. They may be divided into three main groups:

(1) **Sugars** (glucose or grape sugar, cane sugar, milk sugar, etc.).

(2) **Starch** (potato starch, wheat starch, rice starch, etc.).

(3) **Cellulose** (forming the main structure of plant cell membranes and tissues, and represented in manufactured products by cotton, linen, paper and some kinds of artificial silk).

**Cane sugar.**—This important sugar, which has the formula  $C_{12}H_{22}O_{11}$ , is obtained principally from the juices of the sugar cane and sugar beet (Fig. 313). The *sugar cane* contains about 17 per cent. of sugar, which is obtained by crushing the cane between rollers to obtain the juice, making this juice slightly alkaline with lime, clarifying, evaporating in vacuum pans, and

refining the crystals. The Indian cane and the preparation of a kind of 'honey' from its juice became known in Europe during the Indian conquest by Alexander the Great in 327 B.C. In Egypt, in 1000 A.D., the sugar industry was highly developed.



SUGAR BEET.



SUGAR CANE.

FIG. 313.

That the *sugar beet* contained a sugar identical with that obtained from the cane, was discovered by the German chemist Marggraf in 1747. The percentage of sugar in the beet was then about 6, but by special methods of cultivation it has now been raised to from 13 to 16 per cent. In the extraction of sugar from the beet, the root is sliced and the sugar extracted by water in what is known as the *diffusion process*, i.e., the sugar is allowed to diffuse out through the cell walls of the tissue into water outside, whilst the non-diffusible impurities in the sap remain in the cells. The solution is heated with a little lime, and the excess of lime removed by carbon dioxide. The liquid is filtered, a little sulphur dioxide is added, and the clear sugar solution evaporated in vacuum pans and crystallised. The sugar is purified by decolorising with charcoal (p. 409), and recrystallised. The uncrystallisable residue from the cane juice is **molasses** or **treacle**; that from the beet is not suitable



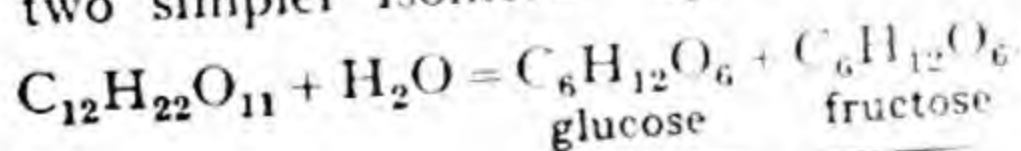
for food, but since it is rich in potassium salts it has been worked up for use as a fertiliser. Some sugar residues are also fermented for the production of alcohol: **rum** is a spirit obtained from molasses by fermentation and distillation. Treacle contains about 45 per cent. of cane sugar, about 7 to 8 per cent. each of the sugars glucose and fructose (*q.v.*) and 8 per cent. of mineral matter.



FIG. 314.—A FIELD OF SUGAR CANE.

When cane sugar is carefully heated it melts at  $160^{\circ}$  and on cooling an amorphous glass of **barley sugar** is formed. When heated at about  $200^{\circ}$ , sugar loses water and is slowly converted into a deep brown, soluble mass called **caramel**, used for colouring soups, etc. When heated more strongly the sugar swells up, chars, and evolves gases and water, leaving a residue of carbon.

When cane sugar is boiled for some time with very dilute acid, it takes up the elements of water and is hydrolysed into a mixture of two simpler isomeric sugars, called **glucose** and **fructose**:



invert sugar.

The hydrogen ion of the acid acts as a catalyst. The mixture of glucose and fructose is called **invert sugar** because the solution now rotates the plane of polarised light to the left, whereas cane sugar rotates it to the right (p. 514). Cane sugar is generally called **sucrose** in chemistry; all sugars have chemical names ending in *-ose*.

**Glucose.**—This sugar,  $C_6H_{12}O_6$ , which is sometimes called **grape sugar** because it occurs in grapes (and in other ripe fruits),

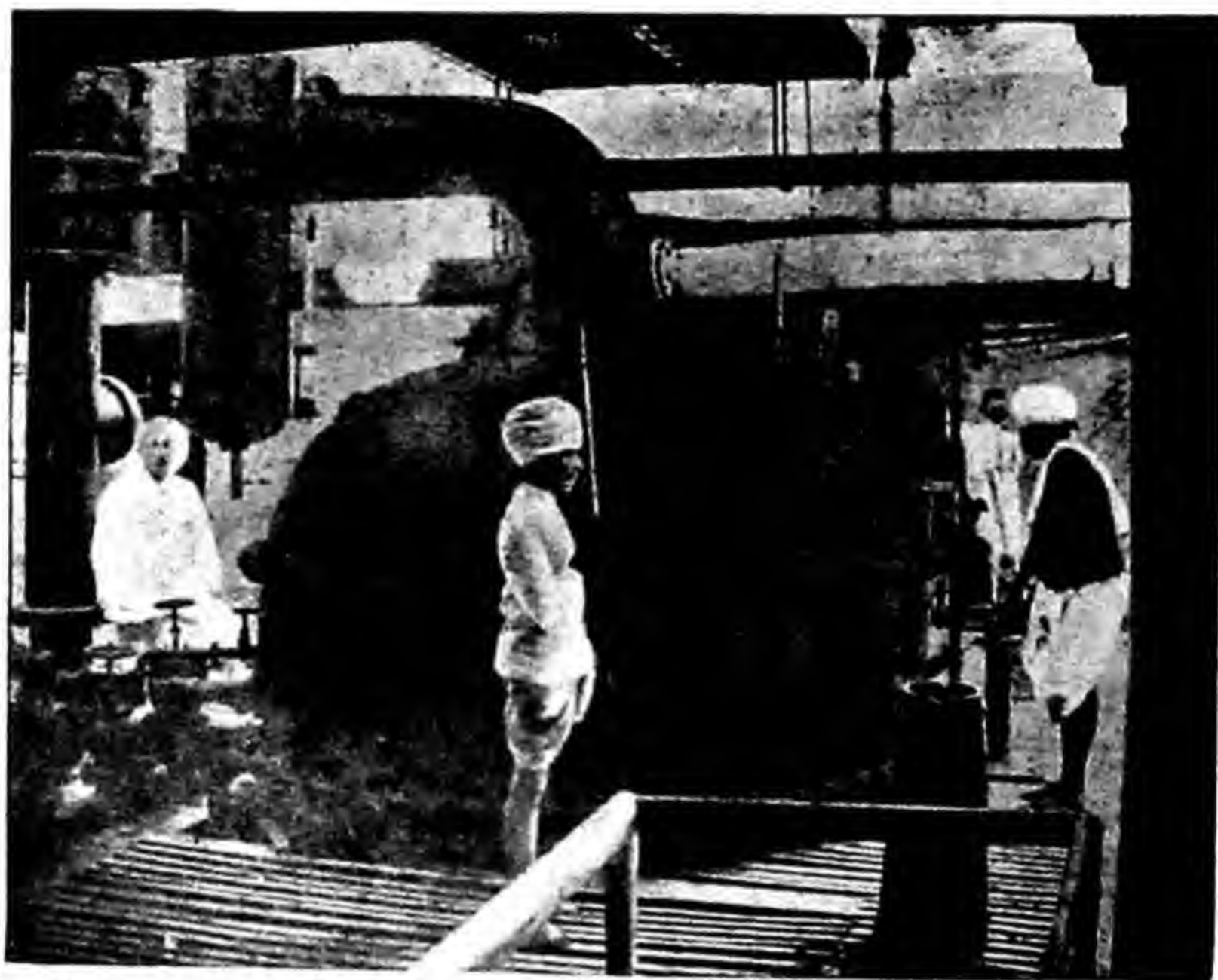
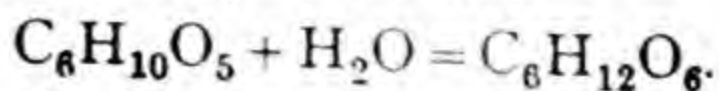


FIG. 315.—VACUUM PAN EVAPORATING SUGAR CANE JUICE TO OBTAIN RAW SUGAR.

is present in honey, together with **fructose**. When honey, which is at first liquid, is allowed to stand the glucose gradually crystallises and the honey 'sets.' Glucose crystallises with much greater difficulty than cane sugar; fructose is still more difficult to crystallise and remains liquid in the honey when most of the glucose has crystallised out.

Glucose is manufactured on the large scale for use in jams, etc. (although it is not so sweet as cane sugar), by boiling starch with a dilute acid, when hydrolysis occurs:





The acid is neutralised and the liquid evaporated, when a hard crystalline mass of glucose is obtained. A liquid solution containing glucose and dextrin (*q.v.*), manufactured on the large scale in America, is known as *corn syrup*.

Glucose is abnormally present in urine in diabetes: **fructose** is manufactured for use by diabetic patients in place of cane sugar by heating **inulin**, a starch present in dahlia tubers and chicory roots, with dilute acid.

**Milk sugar**, or **lactose**,  $C_{12}H_{22}O_{11} + H_2O$ , occurs in milk: it is much less soluble and less sweet than cane sugar and is used in feeding infants. **Maltose**,  $C_{12}H_{22}O_{11} + H_2O$ , isomeric with lactose, is formed by the action of the enzyme diastase upon starch in the germination of grain, and is therefore formed in malt (*q.v.*). **Raffinose**,  $C_{18}H_{32}O_{16} + 5H_2O$ , is a tasteless sugar found in sugar beets.

**Starch**.—The most abundant of all foods obtained from plants is starch. It occurs in all green plants, but principally in the seeds of grains and in potato tubers. If wheat flour is tied up in a linen bag and kneaded with water, a milky liquid runs through, which on settling deposits starch, and a sticky mass of **gluten**, a protein (p. 404), containing nitrogen, remains in the bag. Rasped potatoes when stirred up with water also give a milky liquid containing starch.

Various kinds of starch are distinguished, according to the source, *e.g.*, wheat, maize, rice and potato starch. Rice starch

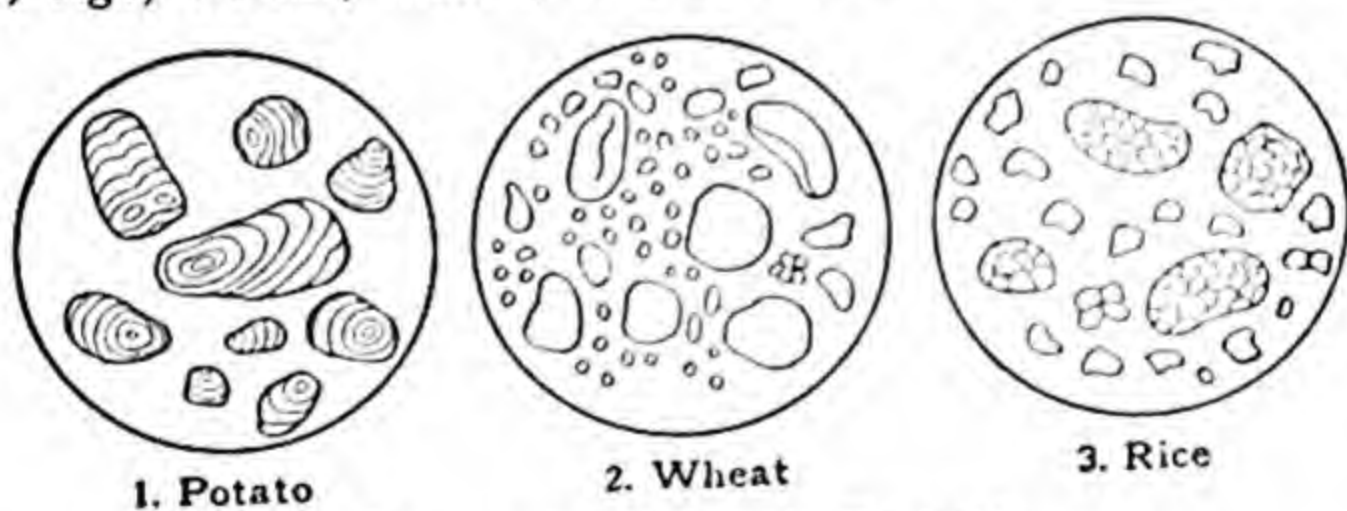


FIG. 316.—STARCH GRAINS.

is mostly used for laundry work; maize starch is *cornflour*. The varieties of starch are distinguishable under the microscope (Fig. 316): rice starch forms the smallest granules ( $1/3000$  in.) and potato starch the largest ( $1/300$  in.). Starch granules are insoluble in cold water, but in hot water they swell up and burst, and the starch forms a *colloidal solution*. This gives a blue colour with iodine, which also stains starch granules, *e.g.*, in

plant cells. The empirical formula of starch is  $C_6H_{10}O_5$  but the molecule is more complex. When heated at about  $210^\circ$ , or when moistened with very dilute nitric acid, dried, and heated at  $100^\circ-125^\circ$ , starch is converted into dextrin, with the same empirical formula as starch, but soluble in *cold* water to form a thick gummy solution (*British gum*). The gloss on starched and ironed linen is due to the formation of a layer of dextrin. There seem to be several kinds of dextrin, coloured blue, or red, or not coloured at all, by iodine. Starch foods are probably partly converted into dextrans on cooking.

Natural gums are closely related to dextrans; for example *gum arabic*, an exudation from tropical acacias, is principally the calcium and potassium salts of arabic acid, which has the formula  $C_{12}H_{22}O_{11}$ . Another similar substance found in fruits is pectin: this causes the gelatinisation of fruit juices (*e.g.*, red currant jelly). Pectic substances are also present in several algae and lichens.

Unripe fruits contain protopectin (or pectinogen), which gives them rigidity. As the fruit ripens, an enzyme, pectosinase, hydrolyses the protopectin into pectin and a cellulose. Boiling with water or dilute acids causes the same change. Pectin is soluble in water, giving a colloidal solution; in the presence of sugar and some acid (present in fruit juices), it forms a jelly. Pectin is found in all vegetable tissues, particularly in fruits and in turnips, carrots and sugar beets. The value of a fruit for jam-making depends on its pectin content. Large quantities of pectin are manufactured from sugar beet residues, from the inner peel of lemons and oranges and from apple waste. Pectins have a certain food value when in association with proteins and fat. Pectin is the methyl ester (p. 518) of pectic acid, which is formed from it by a process of hydrolysis in over-ripe fruits or by heating pectin solutions at a high temperature. It does not form a jelly.

Agar and Irish moss contain calcium salts of an organic ester of sulphuric acid. Iceland moss is a very complicated mixture of substances. Algin, obtained from seaweed (p. 335), consists chiefly of an insoluble alginic acid, the antimony salt of which can be used to preserve fabrics against moths. Other salts are used in waterproofing. Norgine is a commercial algin; when treated with formaldehyde vapour it yields a product insoluble in boiling water.

In bread-making the wheat flour is mixed with water, a little salt (mashed potatoes are sometimes added), and a little yeast (*q.v.*). On standing in a warm place the small amount of sugar



present in the flour is fermented and bubbles of carbon dioxide are formed, inflating the dough and rendering it porous. The gluten in the flour becomes softened and partly disintegrated. The mass is kneaded to press out some gas, divided into loaves, and baked. The porous character is preserved. The heat kills the yeast and stops the fermentation, and most of the alcohol formed in the fermentation escapes. Part of the starch is converted into dextrin, especially on the crust. The loaf is nearly half water and, contrary to common belief, the water content does not alter very much when the bread becomes 'dry,' or 'stale,' on standing. If stale bread is rebaked for a time in a closed tin it becomes soft like new bread.

Poor flour may be bleached with chlorine, nitrogen peroxide, or nitrogen chloride; when it does not make satisfactory bread, 'improvers' are added, consisting of calcium phosphate, potassium and ammonium persulphates or benzoyl peroxide. Alum is not often used in England, but it seems to be regarded as permissible in America. 'Self-raising flour' is a mixture of flour and baking powder, *i.e.*, flour with sodium bicarbonate and an acidic substance, such as tartaric acid, cream of tartar, acid phosphate of potassium or calcium, acid sodium pyrophosphate, and, occasionally, acid sodium sulphate. In America, alum appears to be used as the acidic substance, but in England it would be regarded as deleterious. ('Egg substitute' is merely baking-powder coloured yellow). Instead of wheat flour, rye is largely used in Germany; Indian corn meal does not make good bread. Oatmeal and rice do not form bread.

**Sago** is a starch obtained from the pith of the stems of several species of palm growing in the Malay Archipelago, the Philippine Islands, and parts of India. **Tapioca** is a similar product (*cassava starch*) obtained from the root tuber of a tropical plant. In the fresh state this plant contains or yields the very poisonous hydrocyanic acid, but this is eliminated on drying. **Arrowroot** is a starch from the tubers of a West Indian or Jamaican plant. **Glycogen**, or **animal starch**, is a colourless amorphous powder present in the livers of mammals (p. 553).

**Cellulose.**—The walls of young cells of plants are composed mainly of the carbohydrate cellulose, which is isomeric with starch,  $(C_6H_{10}O_5)_n$ , but differs from it by being insoluble even in boiling water and in being indigestible (but see p. 542). *Cotton* and *flax* are almost entirely cellulose (Fig. 317), and filter paper is nearly pure cellulose.

**Paper.**—In woody fibre the cellulose exists in combination with lignin,  $C_{19}H_{22}O_9$ ; in flax the cellulose is combined with pectin. From woody fibre the lignin is dissolved out by certain reagents, leaving the cellulose, which is made into paper. The wood is chopped or ground and boiled ('cooked') with caustic soda solution, or more usually for cheap paper with solutions of calcium bisulphite,  $Ca(HSO_3)_2$ , or a mixture of sodium sulphide,  $Na_2S$ , and sodium sulphate. The lignin and other constituents are removed and a

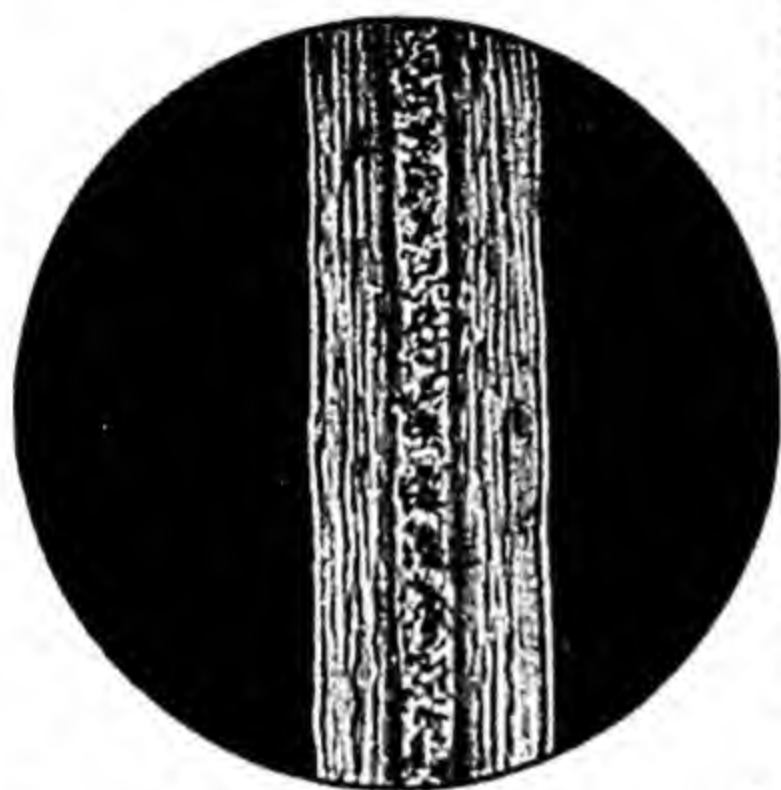


FIG. 317.—SECTION OF A COTTON FIBRE.

pulp of cellulose remains, which is washed and bleached with sodium hypochlorite or bleaching powder solution without the addition of acid. If intended for writing paper, the pulp is *sized* by adding rosin soap and alum, which form an insoluble aluminium resinate which becomes glossy on hot-rolling. Gypsum, china clay, or other white insoluble substances are added as 'fillers' or 'loaders,' and a smooth surface may also be produced by casein, a protein obtained from milk (*q.v.*). The pulp is then formed into sheets by special machinery, and these sheets are passed through hot rollers. The finest quality of paper is the old-fashioned kind produced from the cellulose of linen rags.

Paper is also made from esparto grass, straw, and bamboo. Much modern paper is of very inferior quality and raw wood pulp is sometimes used to make a very poor paper. The oldest kind of paper is the Egyptian *papyrus*, formed from the sliced stems of the papyrus plant (*Cyperus papyrus*), gummed together in two layers with the sections at right angles. It was in use at least as early as the Third Dynasty (2900 B.C.), although the oldest actual specimen is of the Eleventh Dynasty (2000 B.C.). The writing was done with a carbon ink with reed pens. Papyrus was also used by the Greeks and Romans, who used metal pens (not split): quill pens are first mentioned by Isidore of Seville (630 A.D.).



Cotton or cellulose is insoluble in a boiling solution of caustic soda, whilst wool (p. 501) dissolves. If a piece of 'shoddy' is boiled with soda, the wool dissolves and any cotton will remain.

Whilst cellulose is resistant to enzymes (natural ferments), an anaerobic organism in the soil decomposes it rapidly, and this fact has been utilised in the production of artificial farmyard manure from garden refuse to which nitrogenous matter has been added.

**Cellulose products.**—A concentrated solution of caustic soda in the cold converts cotton into **mercerised cotton** (invented by John Mercer in 1844), which is lustrous like silk and more easily dyed than ordinary cellulose.

The natural cotton fibre is flat, like a ribbon (Fig. 317), whilst the fibres of silk and of mercerised cotton are cylindrical and reflect light more easily, hence they appear lustrous (Fig. 318). Mercerised cotton contains cellulose hydrate.

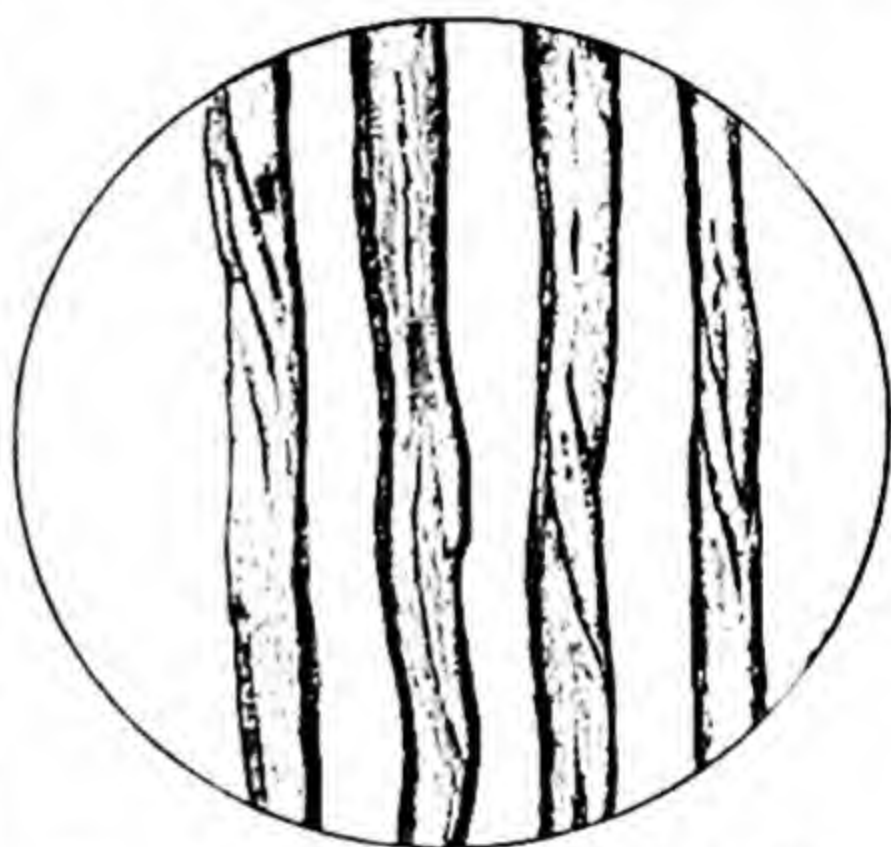


FIG. 318.—MERCERISED COTTON.

When treated with *cold* concentrated sulphuric acid, cellulose is *not* charred but forms a pulpy mass and gradually dissolves. The solution on dilution and boiling yields glucose. The

cellulose is more easily dissolved by *very* concentrated hydrochloric acid. From glucose, alcohol is obtained by fermentation (*q.v.*) and this process may be important in the future for the production of power alcohol.

When sheets of paper are passed through cold, slightly diluted sulphuric acid and then washed, **parchment paper** is formed. This is impervious and is used for tying over jam jars, etc. It consists of cellulose covered with a superficial layer of **amyloid**.

**Nitrocellulose** is produced by treating cellulose (cotton) with a mixture of concentrated nitric and sulphuric acids. It is not a mixture of concentrated nitric and sulphuric acids. It is not a nitro-compound (containing the radical  $-\text{NO}_2$ ) but a nitrate, or cellulose ester, containing the group  $-\text{NO}_3$ : it is cellulose **nitrate**. *Gun cotton*, discovered by Schönbein in 1845, is one variety: it is insoluble in a mixture of alcohol and ether, but

another nitrocellulose called *collodion cotton* is soluble, and the viscous solution, called *collodion*, is used in surgery because it leaves by evaporation a thin waterproof film on any surface. A mixture of collodion cotton and camphor pressed into moulds is *celluloid*: it is very inflammable and burns fiercely on ignition, even under water, since the material contains all the oxygen requisite for combustion, in the form of  $\text{NO}_2$  groups. Nitrocellulose explosives, and nitrocellulose lacquers will be described later. Other important cellulose derivatives are the different varieties of artificial silk.

**Artificial silk.**—There are several varieties of this, all quite different from real silk:

(i) **Viscose silk**: mercerised wood cellulose when treated with carbon disulphide forms a compound called *cellulose xanthate*, which dissolves in alkali to form a solution known as viscose. This solution is squirted under pressure into an acid solution, when a thread of cellulose is precipitated. Viscose silk is, therefore, a cellulose fibre. It is resistant to alkalies, so that it can be woven together with unbleached cotton and the fabric bleached and dyed in the piece.

(ii) **Cuprammonium cellulose**: cotton dissolves in the deep blue solution formed by dissolving cupric oxide in ammonia. On squirting into dilute acid, the solution deposits a thread of cellulose. This process is not very much used, but the solution is used in waterproofing canvas, an impervious layer of cellulose being deposited on the porous fabric. Canvas so treated is also less liable to rot.

(iii) **Nitrocellulose** is dissolved in alcohol and ether and the solution squirted into water. The nitrocellulose thread is 'denitrated,' or converted into cellulose, by treatment with a reducing agent, such as ammonium sulphide.

(iv) **Cellulose acetate**, a cellulose ester also used as aeroplane wing dope, is obtained by acting on cellulose with acetic anhydride and acetic acid, and the solution in acetone is squirted into warm dry air. Acetate silk was formerly difficult to dye, but it may now be dyed by special methods in various colours.

The artificial silk industry has reached enormous proportions in recent years.

By mixing cellulose acetate with camphor or camphor substitutes, a substitute for celluloid (in turn a substitute for ivory), called **cellon**, is obtained, which has the valuable property



of being non-inflammable. It is more elastic than celluloid and is used in making bristles for hair brushes, for the production of imitation horse-hair, and of non-inflammable cinematograph films. In the form of a viscous solution it is used as a varnish for wood, paper, and metal, for enamelling aeroplanes and as an electric insulator. Nitro-cellulose when mixed with linseed oil and spread on cotton fabric, yields an 'artificial leather,' which may be passed through embossed rollers to give it a grain. It is largely used for furniture and motor-car upholstery as 'rexine,' etc.



FIG. 319.—SILK FIBRES.

**Silk and wool.**—True silk is a different material altogether from artificial silk, so that the latter is not really a good name—it is 'imitation silk.' True silk in the natural state, as spun by the silkworm, consists of a double fibre of a substance called fibroin, a protein (p. 404),

cemented together into one thread by a gummy material called sericin. The raw silk is boiled with soap, when the sericin dissolves and the two fibroin threads separate (Fig. 319). Silk has a great affinity for metallic salts, and since it is sold by weight it is usually treated with such things as tin phosphate. Black silk may contain four times as much metal salt as silk. The strength of the silk is impaired by this treatment, which is a misuse of chemistry.



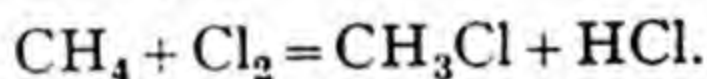
FIG. 320.—WOOL FIBRE.

**Wool** is chiefly composed of fibres of a protein (*q.v.*), **keratin**, which is also the principal constituent of horn, claws, nails,

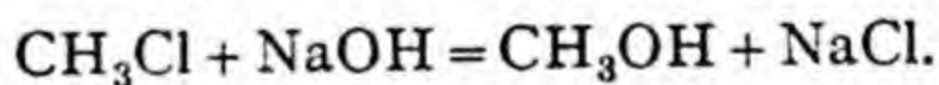
feathers, and hair (Fig. 320). It contains fairly large amounts (up to 5 per cent.) of sulphur. **Chitin** is a protein constituent of the shells of lobsters, crabs, and beetles: its formula is  $C_{30}H_{50}O_{19}N_4$ . **Mucin** is a protein which gives the viscous character to saliva and other body fluids: it occurs in large quantities in snails, although several varieties exist, and its composition is rather indefinite.

**The preservation of timber.**—This is carried out by impregnating the wood with antiseptic liquids which prevent the action of bacteria in bringing about decay. Various substances—tar oils, creosote (containing phenol and cresols, p. 523), mercuric chloride, copper sulphate, and fluorine compounds (sodium fluoride, etc.), are all in use, and the substance may be forced into the material of the wood by exposure to vacuum followed by pressure.

**Alcohol.**—Common alcohol is one of a group of several substances all of which contain the **hydroxyl group**,  $-OH$ , in combination with the radical of a hydrocarbon. The simplest alcohol is **methyl alcohol**. When methane is treated with chlorine, substitution occurs (p. 439) and **methyl chloride**, containing the radical methyl,  $-CH_3$ , in combination with chlorine, is formed:

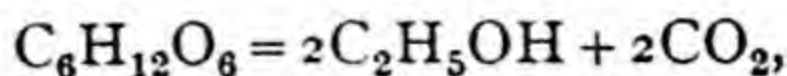


When methyl chloride is boiled with caustic soda solution, the chlorine is replaced by the hydroxyl group and methyl alcohol is formed:



Common alcohol is **ethyl alcohol**,  $C_2H_5OH$ , the **ethyl radical**,  $C_2H_5$ , being derived from the hydrocarbon ethane,  $C_2H_6$ . The  $OH$  group in alcohols is not ionisable, so that they do not behave as bases. **Glycerin** is also an alcohol, but it contains *three* hydroxyl groups: it is derived from the hydrocarbon propane,  $C_3H_8$ , and is  $C_3H_5(OH)_3$ : its correct name is **glycerol**, the ending *-ol* denoting an alcohol.

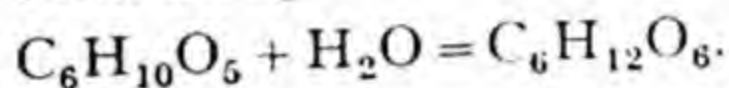
The oldest known alcohol, ethyl alcohol, which is usually simply called 'alcohol,' or 'spirit of wine,' is contained in fermented liquors, such as wine and beer, and may be obtained from them by fractional distillation. Brandy is so obtained from wine. Alcohol is obtained for industrial purposes by the fermentation of glucose by means of yeast. The reaction is:





although it almost certainly takes place in stages (p. 509), and small quantities of other substances, such as amyl alcohol (*fusel oil*, giving bad whisky its deleterious properties), are also produced. The carbon dioxide is evolved in bubbles from the mass of the liquid, and the name fermentation is derived from the Latin *fervere*, to boil: the name yeast is said to be derived from a Teutonic root *jeson*, to froth.

Molasses may be fermented to yield a distilled product, *rum*, and considerable quantities of industrial alcohol are obtained from starch, in the form of grain, potatoes, etc. The starch may be converted into maltose and dextrin by mashing the material to a pulp and adding malt, which is made by allowing moist barley to sprout and then drying in kilns. The malt contains an **enzyme** (a catalyst produced by a living organism) called **diastase**, or **amylase**, which causes starch to add on the elements of water to form a sugar:



When the diastase has completed its work, another ferment or enzyme, **zymase**, is added in the form of yeast, and this converts the sugar into alcohol and carbon dioxide.

**Enzymes.**—**Yeast** consists of minute living plant cells which secrete the enzyme zymase. Cane sugar ferments more slowly than glucose, because it must first be hydrolysed to glucose and fructose (*invert sugar*, *q.v.*) by another enzyme in yeast, viz. **sucrase** (or *invertase*). The invert sugar is then fermented by the zymase.

Milk sugar cannot be fermented at all by yeast, but enzymes in bacilli present in milk will convert it into **lactic acid**, which is the acid present in sour milk. Ferments in micro-organisms contained in cheese will convert milk sugar into **butyric acid**, to which the unpleasant odour and taste of rancid butter are due.

It appears as though an enzyme generally requires the co-operation of a second substance, called a **co-enzyme**, in order to exert its action, just as some catalysts require promoters (p. 379):

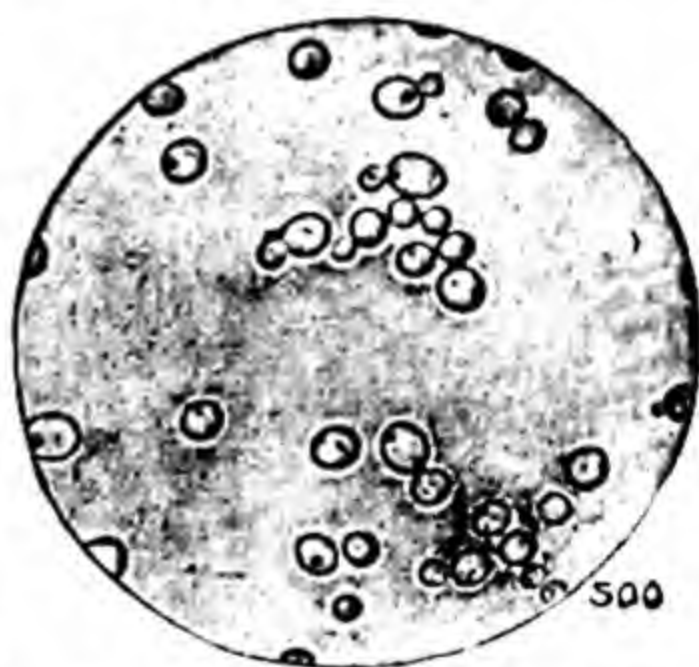


FIG. 321.—YEAST CELLS.  
YEAST IS A UNICELLULAR ORGANISM WHICH IS PROPAGATED BY DIVISION. SOME OF THE CELLS SHOWN ARE "BUD-DING."



the inactive form of the enzyme is often called a *zymogen*; it may sometimes be activated by acids or alkalies, or sometimes requires the action of a co-enzyme called a *kinase*. Pepsinogen is activated into pepsin by hydrochloric acid (p. 551); trypsinogen is activated by enterokinase (p. 553). Rennin (p. 544) is secreted as a zymogen and activated by hydrochloric acid.

Enzymes differ from ordinary inorganic catalysts in being gradually destroyed in their action (perhaps by other enzymes or similar substances), in being rendered inactive by too high a temperature (above  $50^{\circ}$  usually) and also sometimes by the products of their action, and in being more specific: an enzyme usually catalyses only one particular reaction.

The modern view that the catalytic activity of all organisms (*e.g.*, yeast cells) is due to secreted enzymes is due to Moritz Traube in 1858. Pasteur, on the contrary, suggested, and vigorously maintained, that fermentation is indissolubly connected with the life-process of the organism: 'no fermentation without life.' In some cases the enzyme, after being elaborated in the organism, is excreted from it, but in others (*e.g.*, in the zymase of yeast) it remains in the cell, where it produces the chemical change.

Enzymes are numerous: a recent treatise gives a list of sixty-one enzymes existing in animal and vegetable tissues and many of them occur in several modifications. Enzymes are nitrogenous substances of a colloidal nature, not necessarily proteins, but resembling them. They readily adsorb other substances and are themselves adsorbed by solids; their chemical nature is still obscure.

Willstätter thinks the molecule of an enzyme consists of a colloidal carrier and a purely chemically active group. The nature of the carrier is variable, since it is possible to separate each enzyme from the chemically defined colloidal companion without loss of activity. Nevertheless, it is not yet possible completely to separate the chemically active groups from the protective colloid without loss of activity.

Recently a 'new' method of converting starch into sugar, and thence into alcohol, which does not require the use of malt diastase, has been used, called the *amylo process*. It has really been used in China from very early times: 'Chinese yeast' contains a mould, *Mucor rouxii*, which (mixed with various materials) is sold as *migen* or *men*. In the process as now carried out chiefly in France, but to a less extent also in Spain,



Italy, and America, the moulds *Rhizopus delemar* and *Mucor boudard* are used. The starchy material (rice, potatoes, etc.) is steeped in water, gelatinised by heating with steam, and the mash treated with the spores of the mould. Growth occurs rapidly and in a few hours yeast is added so that the production



FIG. 322.—EARLY ALCOHOL STILLS SHOWING RUDIMENTARY RECTIFYING COLUMNS (ULSTADIUS, 1526).

of sugar by the mould and its fermentation by the yeast proceed simultaneously.

**Manufacture of alcohol.**—The weak alcohol obtained by fermentation is converted into strong alcohol by fractional distillation. An early type of alcohol still is shown in Fig. 322. At the present day in Great Britain the Coffey still is used for

this purpose (Fig. 323). It consists of two columns, *A* and *B*, called the *analyser* and the *rectifier*, respectively, divided into compartments by shelves with perforations fitted with valves opening downwards, and pipes with the upper end of each an inch or two above the plate so as to retain a thin layer of liquid upon it and dipping at the lower end into a shallow pan on the

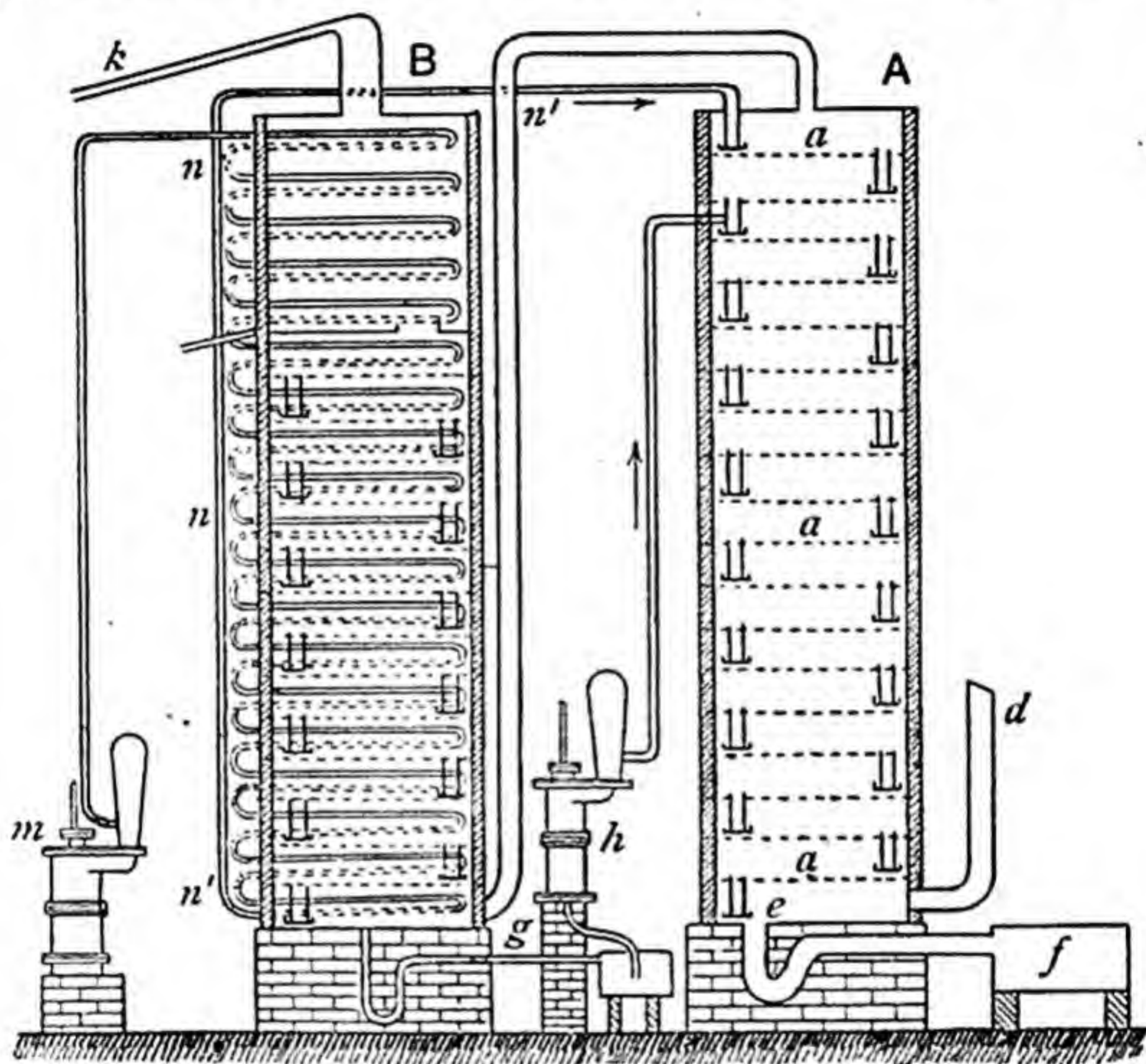


FIG. 323.—COFFEY'S STILL FOR THE MANUFACTURE OF ALCOHOL FROM WEAK ALCOHOLIC SOLUTIONS.

shelf below. Between each compartment and the next is a bend of a long zig-zag pipe, *nnn'*, one end of which is connected with a pump, *m*, delivering the fermented liquor which flows over the compartments *aaa*. Steam is admitted to the analyser at *d* and heats the wash, all the alcohol in which is driven out by the time the spent wash runs out at the bottom at *ef*. The vapour of alcohol and water enters the rectifier at *g*. The strong alcohol vapour passes from *k* to a condenser where the spirit is liquefied. The weak alcohol flows from *B* to the pump *h*, which delivers it to the column *A*.



The strongest commercial alcohol (about 99 per cent.) is called *absolute alcohol*. In order to make industrial alcohol unfit for drinking it is *methyated* by adding crude wood spirit, containing the poisonous methyl alcohol (*q.v.*) and other nauseous ingredients which are very difficult to separate.

In England there are two kinds of methyated spirit: (a) *mineralised methyated spirit*, sold for general use, which is coloured and contains not less than 10 per cent. by volume of wood naphtha (crude methyl alcohol) and in addition not less than 0.375 per cent. by volume of mineral naphtha (petroleum of specific gravity not less than 0.8); and (b) *industrial methyated spirit*, which is used for manufacturing purposes and contains not less than 5 per cent. of wood naphtha. The wood naphtha must be sufficiently nauseous to prevent the use of the spirit for drinking purposes.

A wine of medium strength may contain  $8\frac{1}{2}$  to 10 per cent. of alcohol, port wine 15 to 20 per cent., sherry up to 21 per cent. Lager or mild ale contains 3 to 5 per cent., stronger ale 5 to 9 per cent., of alcohol. Varieties of brandy and spirits may contain 30 to 40 per cent. of alcohol, cognac 50 per cent. or more. The strengths of alcoholic liquors for revenue purposes, however, are usually expressed in an antiquated manner in terms of the content of 'proof spirit', containing 49.3 per cent. by weight of alcohol: a spirit  $25^\circ$  overproof is such that 100 volumes diluted with water yield 125 volumes of proof spirit; whilst one  $25^\circ$  under proof is such that it contains in 100 volumes 75 volumes of proof spirit. The strength is determined from the specific gravity found by means of a hydrometer.

Alcohol is principally used as a solvent, but it may also be used, especially when mixed with benzene, as a fuel for motor engines. Small amounts are used as a fuel, *e.g.*, in picnic cooking, sometimes in the form of 'solidified alcohol', which is produced by adding cellulose esters or soaps to alcohol.

Ethyl alcohol is an example of a *primary alcohol*, which contains the group  $-\text{CH}_2\text{OH}$ . A *secondary alcohol* has the group  $=\text{CH}\cdot\text{OH}$ , and a *tertiary alcohol* the group  $\equiv\text{C}\cdot\text{OH}$ .  
*Eg.*,

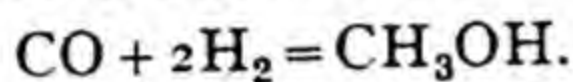
$\text{CH}_3\cdot\text{CH}_2\text{OH}$   
ethyl alcohol

$(\text{CH}_3)_2\text{CH}\cdot\text{OH}$   
*isopropyl alcohol*

$(\text{CH}_3)_3\text{C}\cdot\text{OH}$   
tertiary butyl alcohol

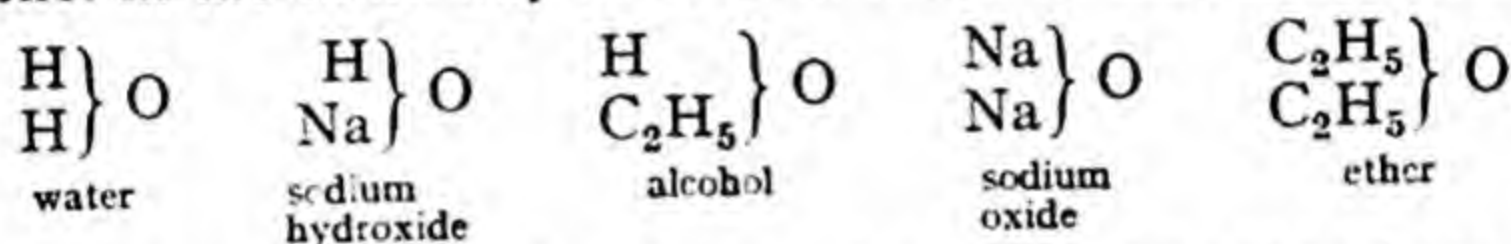
**Methyl alcohol**,  $\text{CH}_3\text{OH}$ , is present in *wood spirit*, which is obtained by distilling wood in retorts. Charcoal, wood tar

(which contains some valuable antiseptics), and a watery liquid containing acetic acid, acetone (which is used as a solvent) and methyl alcohol are formed. This watery liquid is called *pyroligneous acid*. An important synthetic process for the production of methyl alcohol, by passing a mixture of carbon monoxide and hydrogen (water gas, *q.v.*) under high pressure over a catalyst such as zinc oxide, has recently been developed on the large scale by Patart in France :



Methyl alcohol is principally used as a solvent for resins, etc., in making varnishes. It is poisonous and produces blindness. Deaths have been caused by drinking methylated spirit.

**Ether.**—Common ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , is *diethyl oxide*, related to alcohol in the same way as sodium oxide to sodium hydroxide :



Ether is prepared by heating a mixture of alcohol and concentrated sulphuric acid at  $140^\circ$  and running in alcohol. It distils over and is purified by washing with water, drying over calcium chloride, and redistilling. Ether is a very volatile, mobile liquid, with a very strong pleasant odour ('ethereal odour'). The vapour is very inflammable. It is used as an anaesthetic. The liquid is used as a solvent for oils, fats, and resins, chiefly in pharmacy, and a mixture of ether and alcohol is used as a solvent for nitrocellulose (p. 499).

**Fermentation.**—The production of alcohol and carbon dioxide from sugar by the action of yeast is one example of an important group of similar reactions. Pasteur, who showed that the fermentation of sugar is associated with the living yeast plant, and that in the souring of milk, the milk sugar is converted into lactic acid by a bacillus (which acts similarly on glucose), considered, as has been stated, that *all* cases of fermentation were brought about by living organisms : 'la fermentation est le résultat de la vie sans air.' Even in his day, however, fermentation processes occurring without living organisms were known, viz., the conversion of starch into sugar by *diastase*, roughly isolated by Payen and Persoz in 1833 ; the splitting of a substance, amygdalin, in bitter almonds into glucose, benzaldehyde ('oil of bitter almonds') and hydrocyanic acid by a non-living (unorganised) ferment called *emulsin*, present in the almonds,



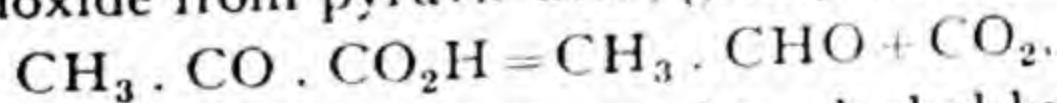
and recognised by Liebig and Wöhler in 1832; the digestion of proteins by the pepsin of the gastric juice (recognised by Eberle and Schwann in 1836); and the splitting of cane sugar by sucrase.

Traube's theory of fermentation assumes that even when living organisms bring about the change, it is the *enzymes* which they secrete which are the active agents, and Pasteur's theory in its narrow form is now abandoned. Ferments are chemical agents, *catalysts*, which initiate and cause certain definite chemical reactions. The modern theory was accepted chiefly as a result of experiments of Buchner in 1897: he showed that when yeast cells were disintegrated by trituration and pressure, a juice was obtained which brought about alcoholic fermentation (because it contained the enzymes secreted by the yeast) but was quite free from living cells.

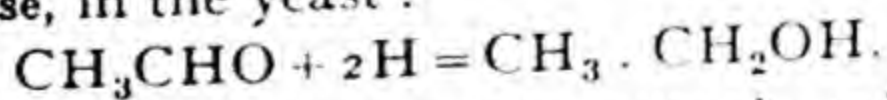
Just as is the case with ordinary catalysts, very small amounts of ferments will bring about the alteration of very large amounts of the substances on which they act, but in the end they become inactive. They are readily *adsorbed* from solutions by many solids, are precipitated from solution by alcohol or certain salts, and are rendered inactive at temperatures of  $60^{\circ}$ - $70^{\circ}$  when in solution but in the dry state are still active after heating to  $120^{\circ}$ - $150^{\circ}$ .

The activity of the ferment generally appears only in presence of a *coenzyme* (p. 503), and of acidity (*e.g.*, with pepsin) or alkalinity (*e.g.*, with trypsin); in the case of zymase Harden has shown that a phosphate is also requisite, and the necessary phosphate-containing material is present in yeast juice. Ferments bringing about oxidation, *oxidases*, are present in vegetable and animal bodies: these also contain a ferment, *catalase*, which rapidly decomposes hydrogen peroxide, as is seen by the effervescence produced when this substance is used in disinfecting a bruised part of the skin, or a wound. Plants also contain the enzymes diastase, maltase, and protease (splitting proteins).

Yeast contains an enzyme, *carboxylase*, capable of splitting off carbon dioxide from pyruvic acid, giving aldehyde (p. 510):



and the aldehyde may then be reduced to alcohol by a reducing enzyme, *reductase*, in the yeast:

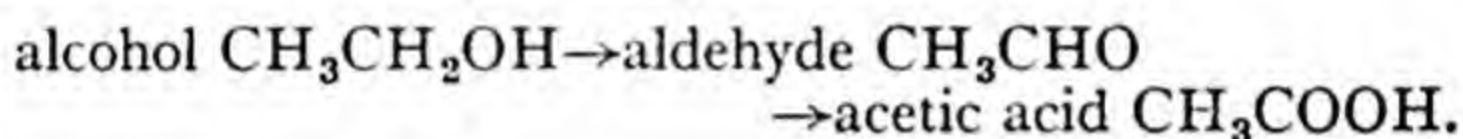


The conversion of the glucose into pyruvic acid is a missing link.

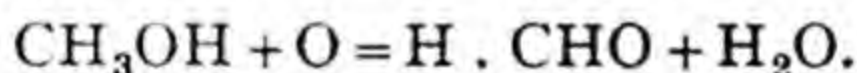
**Acetone ; aldehydes.**—Methyl alcohol, an organic acid, viz. acetic acid, and a neutral substance called acetone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ , are produced by the distillation of wood (p. 407). Acetone is what is called a **ketone**, containing the **carbonyl group**,  $-\text{CO}-$ , in combination with two radicals.

Acetone and normal butyl alcohol,  $\text{C}_3\text{H}_7 \cdot \text{CH}_2\text{OH}$ , are made for use as solvents for nitrocellulose by the **Weizmann process**. In this, a mash prepared from grain is sterilised, inoculated with a culture of *Bacillus granulobacter*, and fermented. Hydrogen and carbon dioxide are evolved, and a mixture of acetone and about twice its weight of butyl alcohol is obtained by distillation. Recently, synthetic butyl alcohol obtained from acetylene has come into the market from Germany. Acetone is also made by distilling calcium acetate, so that acetic acid may be converted into acetone.

Alcohol on oxidation yields acetic acid,  $\text{CH}_3\text{COOH}$  (*q.v.*), but the process may be arrested at an intermediate stage, viz. the substance **acetaldehyde**,  $\text{CH}_3\text{CHO}$  :



When methyl alcohol vapour and air are passed over heated copper, oxidation occurs, and **formaldehyde**,  $\text{H} \cdot \text{CHO}$ , is produced



It contains the characteristic **aldehyde group**,  $-\text{CHO}$ , also present in acetaldehyde, which is obtained by oxidising ethyl alcohol with sulphuric acid and potassium dichromate, and is also present in the first fractions in the manufacture of alcohol (p. 505). Aldehydes are easily oxidised to the corresponding *acids* (*e.g.*, formic and acetic acids).

Formaldehyde, also known as formalin, is used in solution as an antiseptic. From formaldehyde and phenol ('carbolic acid') or similar substances (metacresol, xlenol, etc.), subjected to chemical interaction, a synthetic resin or 'plastic' with the trade name 'Bakelite' is produced. By heat treatment of a mixture of the resin, incorporated with fillers such as wood flour, and colouring matter, under pressure, a rigid, infusible moulding is formed, which is insoluble (except in alkalies) and is an electric insulator. Other synthetic resins are made from formaldehyde and urea  $\text{CO}(\text{NH}_2)_2$  or thiourea  $\text{CS}(\text{NH}_2)_2$ . Other types of plastics are described on pp. 538 and 545. 'Duroprene' is a chlorinated rubber product, the solution of which in



benzene and naphtha is used as a varnish: on evaporation it leaves a resistant film not attacked by acids, alkalies, alcohol, or petrol.

**Nitrocellulose lacquers.**—Butyl alcohol, obtained as described above, is used along with other solvents in the preparation of nitrocellulose lacquers, which are essentially solutions of nitrocellulose in organic solvents together with pigments and substances which confer plasticity and prevent too rapid drying.

In order to produce a solution which is not too viscous, a special type of nitrocellulose is used, which is dissolved, together with gums or resins of various types, to produce the so-called *pyroxylin*

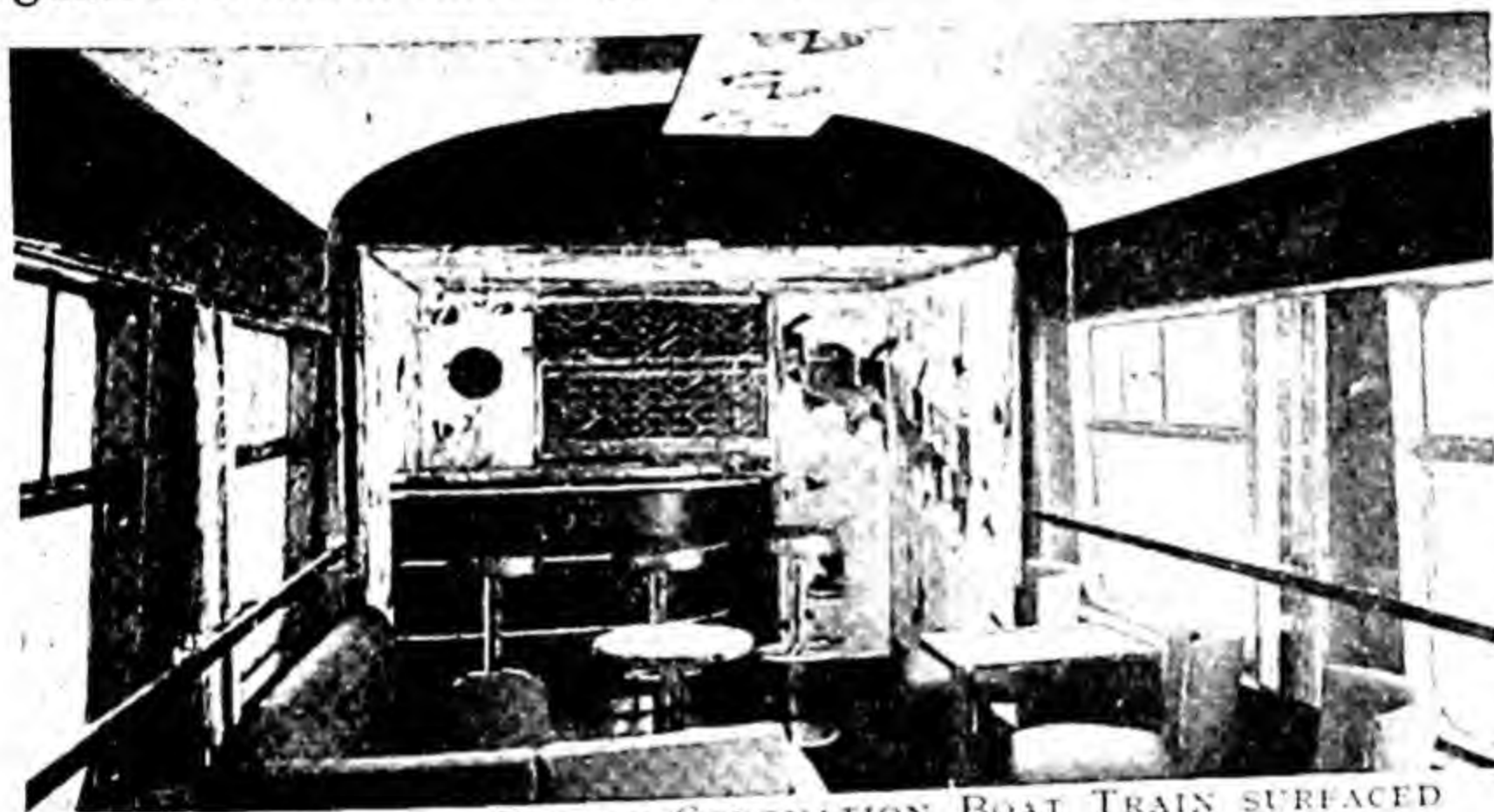


FIG. 325.—LOUNGE BAR OF CORONATION BOAT TRAIN SURFACED WITH 'WAREITE' VENEERED BOARD.

(Bakelite Ltd.)

*lacquer*. This is especially valuable for the 'cellulose finish' of motor-cars, and in making artificial leather. The finish is proof against battery acid, petrol, water, and to some extent against abrasion caused by mud or dust. Many other uses are being found daily for this finish: metal, wood, and glass are all capable of being covered with it, and some varieties can be applied with a brush instead of being sprayed (as is usual in motor finishes). The 'spray gun' is an atomiser working on the principle of the familiar scent spray, compressed air being used. The finish is matt, but may be polished with fine abrasives.

**Organic acids.**—The simplest organic acid, containing the characteristic carboxyl group,  $\text{—COOH}$ , is formic acid,  $\text{H} \cdot \text{COOH}$ ,

discovered in red ants (*Formica rufa*) by Samuel Fisher, whose experiments were reported by John Ray in the *Philosophical Transactions* for 1671. Fisher also prepared lead formate. Formic acid is present in some caterpillars, in bee and wasp stings, and in stinging nettles. Its sodium salt is obtained technically by a process discovered by Berthelot in 1855, viz. by passing carbon monoxide over heated caustic soda or soda lime :



Acetic acid,  $\text{CH}_3\text{COOH}$ , is usually made by the distillation of wood, or by synthesis from acetylene (p. 510). It is present in



FIG. 326.—SECTION OF VINEGAR VAT.

vinegar, obtained by the oxidation of dilute alcohol, such as beer and wine, in presence of air and an organism called *Mycoderma aceti*, a low form of plant which grows on the surface of the liquid.

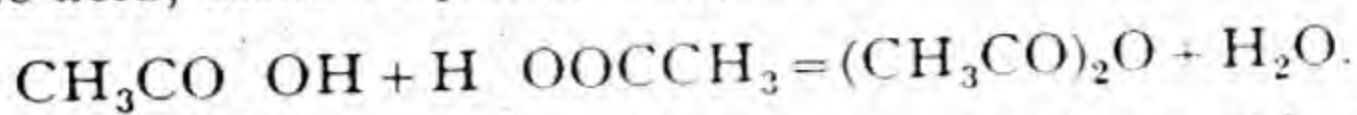
Wine vinegar is made in France by adding wine to a certain amount of strong vinegar in large oak casks provided with openings to admit air and allowing to stand for some days at  $25^{\circ}\text{C}$ . In some cases the cask has a wooden grating on which vine cuttings, stalks, etc., are placed so as to expose a large surface for the growth of the ferment. In making malt vinegar, a *wort*, which is prepared from malt and grain, is

fermented with yeast to produce weak alcohol at a rather higher temperature than is used in making beer. The alcoholic liquid, called *gyle*, is acetified ('quick vinegar process') in a large vat with a perforated shelf upon which rest beech shavings, twigs, or basket work, air entering through holes just above the liquid and escaping through small holes in the top of the vat. The *gyle* is circulated through the vat by sprinkling it over the shavings and raising it again by pumps. The vinegar is allowed to stand for some time to clarify it, and is then filtered. Vinegar contains about 5 per cent. of acetic acid. Vinegar is also made by the acetification of cider.

Concentrated acetic acid, which is obtained from pyroligneous acid (p. 408) by adding milk of lime and distilling the calcium acetate with sulphuric acid, is a liquid of very strong acid smell, which freezes in cold weather and is therefore called *glacial acetic acid*.



By elimination of the elements of water from *two* molecules of acetic acid, acetic anhydride,  $\text{CH}_3\text{CO.O.CO.CH}_3$ , is formed:



It is a liquid with a very irritating odour, used in making some kinds of artificial silk (p. 500).

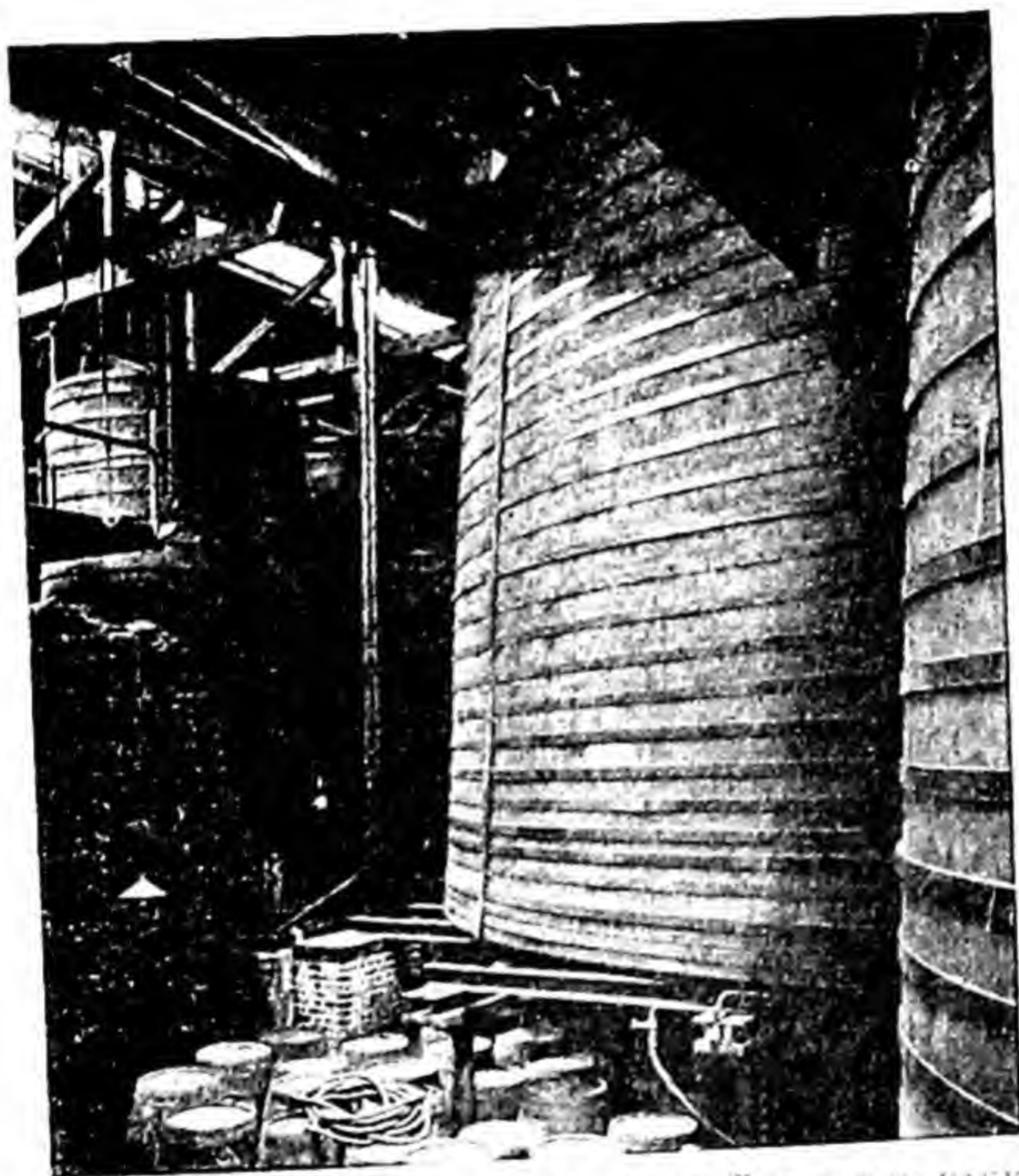


FIG. 327.—VINEGAR VATS AND STACK OF TWIGS FOR PACKING.  
THE LARGE VAT HOLDS 115,000 GALLONS.  
(Crosby & Blackwell)

Oxalic acid,  $(\text{COOH})_2$ , is a dibasic acid; the acid potassium salt,  $\text{KHC}_2\text{O}_4$ , called *salt of lemon* (although lemons contain no oxalic acid), which occurs in wood sorrel, is used in removing ink stains. Calcium oxalate,  $\text{CaC}_2\text{O}_4$ , occurs in crystals (*raphides*) in some plant cells: it is thrown down as a white precipitate when ammonium oxalate solution is added to a solution of a calcium salt (*test for calcium*). Oxalic acid is

made on the large scale by heating sawdust with caustic potash, when the cellulose is oxidised, hydrogen is evolved, and potassium oxalate is formed.

Tartaric acid,  $C_4H_6O_6$ , separates from grape juice during fermentation into wine in the form of the crude acid potassium salt, *argol*, which when purified forms *cream of tartar*,  $KHC_4H_4O_6$ . The acid is prepared from this by precipitating the calcium salt and decomposing it with sulphuric acid. It is used in making baking-powder, effervescent drinks (with sodium bicarbonate), etc. Citric acid is found in many fruits with malic acid (occurring in apples) and tartaric acid, but occurs especially in lemon juice, which contains 6 per cent. of it. Unlike tartaric acid, it does not easily char on heating. A granular mixture of sodium bicarbonate, citric acid, sugar, and a little magnesium salt is sold as *effervescent citrate of magnesia*. Ferric ammonium citrate, used in medicine, forms red scales.

Benzoic acid,  $C_6H_5CO_2H$ , is derived from benzene (p. 522) and is present in gum benzoin. It is prepared by synthetic methods.

**Optical activity.**—Solutions of tartaric acid show the very interesting property of optical activity: they rotate the plane of polarisation of light.

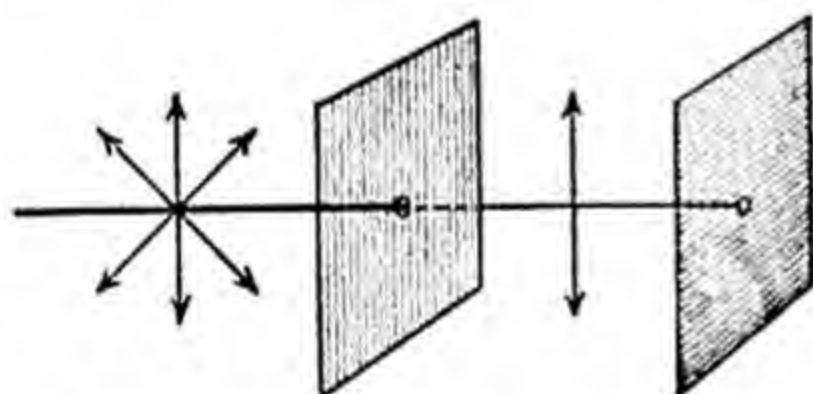


FIG. 328.—POLARISATION OF LIGHT.

In a ray of light there are vibrations at right angles to the direction of the ray, and light consists of so-called *transverse waves*. When the light is passed through certain crystals, such as *tourmaline*, only the vibrations in one plane can pass, and the light is then said

to be polarised. By interposing another crystal with its axis at right angles to the first, these vibrations are also cut out, and no light passes (Fig. 328).

If now an optically active substance, such as a solution of tartaric acid, is interposed between the two crystals, light passes through the second crystal. To produce extinction, this crystal must now be *rotated* through a certain angle. Substances which are optically active thus *rotate the plane of polarisation of light*: some rotate it to the left, some to the right. Each member of an optically active pair rotates the plane of polarisation by an equal amount, but whereas one rotates it to the left the other rotates it to the right. The pair of substances



form enantiomorphs. Two modifications of tartaric acid were recognised by Pasteur (1848); one (ordinary tartaric acid) rotates the plane of polarisation to the right and is called *dextro-tartaric acid*; the other rotates it an equal amount to the left and is called *laevotartaric acid*. An acid which has the same composition as tartaric acid, but is optically inactive, called *racemic acid*, had been discovered in certain kinds of crude cream of tartar from wine by Berzelius in 1829: this was the first recognised case of isomerism. Pasteur prepared sodium ammonium racemate,  $\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_6$  (tartaric acids are

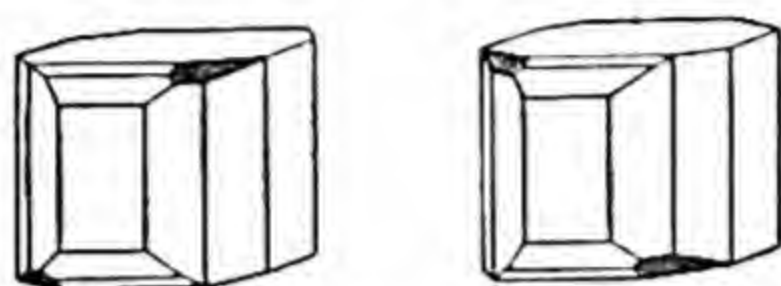


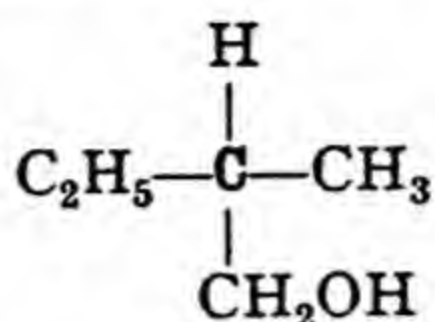
FIG. 329.—CRYSTALS OF DEXTRO- AND LEVO-TARTRATES SHOWING ASYMMETRY OF FACETS (Shaded).

dibasic), and allowed a solution of it to crystallise at a temperature below  $28^\circ$ . He found that two kinds of crystals separated, almost identical in appearance except that one had small facets on its crystals which were in the relation of mirror images to the facets on the others (Fig. 329). These were separated by hand-picking, dissolved separately in water, and the solutions examined with polarised light. One solution rotated the plane of polarisation to the left, the other to an equal extent to the right. When the two solutions were mixed, an optically inactive solution was formed. This was a most important discovery.

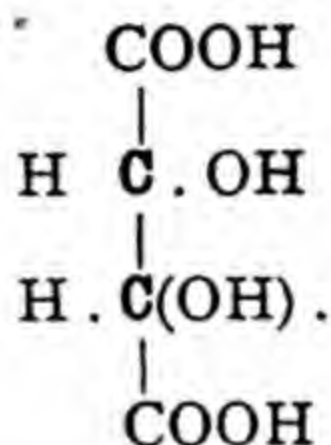
Many other optically active organic compounds besides tartaric acid occur in Nature, such as glucose, fructose, cane sugar, essential oils (*e.g.*, turpentine), and alkaloids. Optical activity seems to be connected with life processes, and frequently only one of the two forms of a substance can be assimilated. Certain moulds or bacilli will feed on one form only, and if grown in a solution containing the two forms, they remove one and leave the other. Pasteur, by growing common mould (*Penicillium glaucum*) on a racemate solution, observed that the salt of the dextrotartaric acid was removed, whilst the laevotartrate present was left unless the process was allowed to go on, when the laevotartrate was also removed.

Optical activity is very commonly due to the presence in a

molecule of an **asymmetric carbon atom**, *i.e.*, one to which four *different* atoms or radicals are attached. Such a compound as the amyl alcohol



contains an asymmetric carbon atom (shown in heavy type), and is optically active. Tartaric acid, as will be seen from the structural formula :



contains *two* asymmetric carbon atoms.

Pasteur's results were explained, on the basis of the asymmetric carbon atom, by van't Hoff and by Le Bel in 1874-75. They assumed that the four valencies of the carbon atom are directed in space towards the four corners of an imaginary regular tetrahedron. If the four corners are occupied by four *different* atoms or groups, two different arrangements of these are possible, the two tetrahedra not being superposable and one is the image of the other in a mirror. They resemble the right- and left-hand gloves or the shoes for the right and left feet. Such **asymmetric** molecules show optical activity.

Besides the *dextro*- and *laevo*-tartaric acids and their inactive combination, racemic acid, there is a third form which is *optically inactive*, because the effect of one tetrahedral half of the molecule is just counterbalanced by the effect of the other : this *internally compensated* inactive acid is called **mesotartaric acid** (Fig. 330).

The carbon atom is not peculiar in producing optical activity : when four *different* groups are arranged about a quadrivalent tin atom, for example, an optically active compound is formed. There are also optically active compounds of silicon, sulphur, and nitrogen.

There is another kind of **space-isomerism**, not, however, causing optical activity, which occurs when the two halves of a molecule



are joined by a double bond (p. 197) so that they cannot rotate. These two forms are called *cis*- (two identical groups adjacent) and *trans*- (two identical groups opposite) isomers.

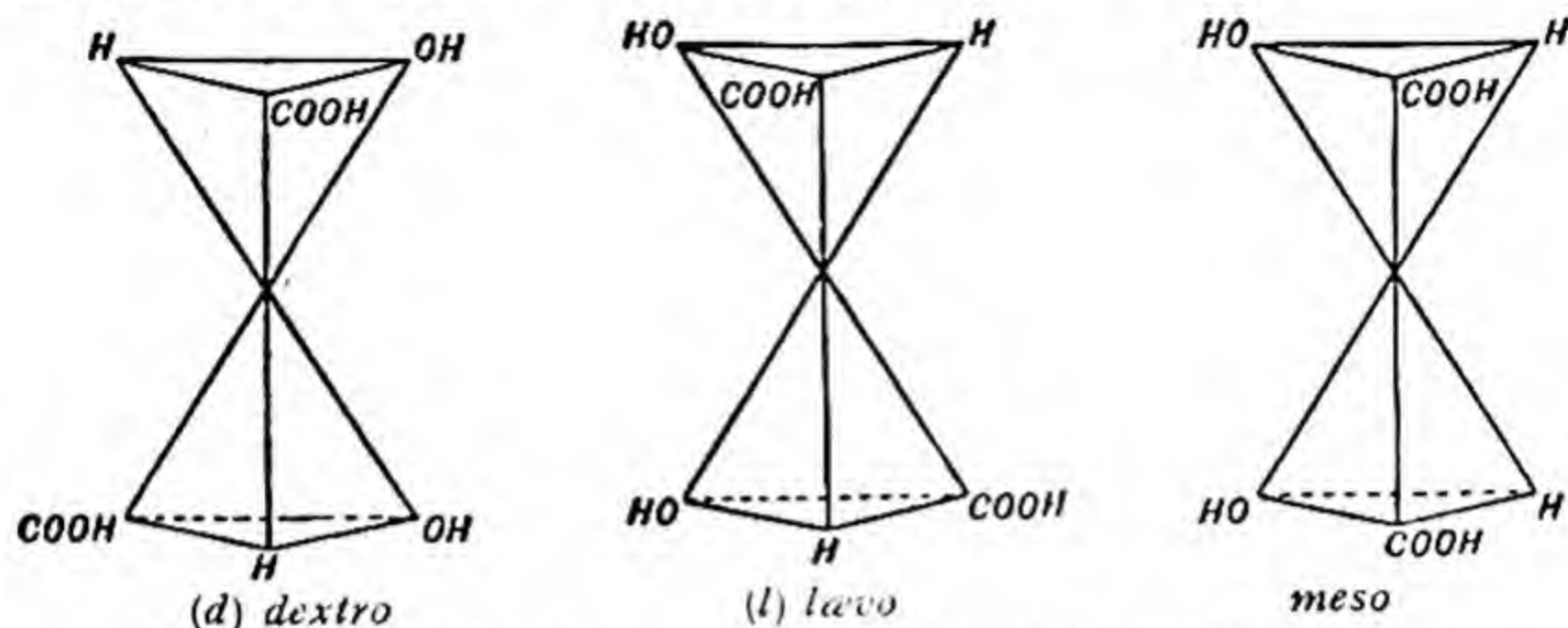


FIG. 330.—OPTICAL ISOMERISM OF THE TARTARIC ACIDS.

EACH MOLECULE CONTAINS TWO ASYMMETRIC CARBON ATOMS, SUPPOSED TO BE AT THE CENTRES OF THE TWO TETRAHEDRA JOINED BY VERTICES. IN THE *d*-FORM THE GROUPS H, OH, CO<sub>2</sub>H SUCCEED ONE ANOTHER IN CLOCKWISE ORDER IN BOTH TETRAHEDRA (LOOKED AT FROM THE SAME ASPECT), IN THE *l*-FORM IN COUNTER-CLOCKWISE ORDER, WHILST IN THE OPTICALLY INACTIVE *meso*-TARTARIC ACID THE ORDER IS CLOCKWISE IN ONE TETRAHEDRON AND COUNTER-CLOCKWISE IN THE OTHER, SO THAT THE MOLECULE AS A WHOLE IS OPTICALLY INACTIVE.

As examples of *cis-trans*-isomers we have two acids called **fumaric** and **maleic acids** (Fig. 331).

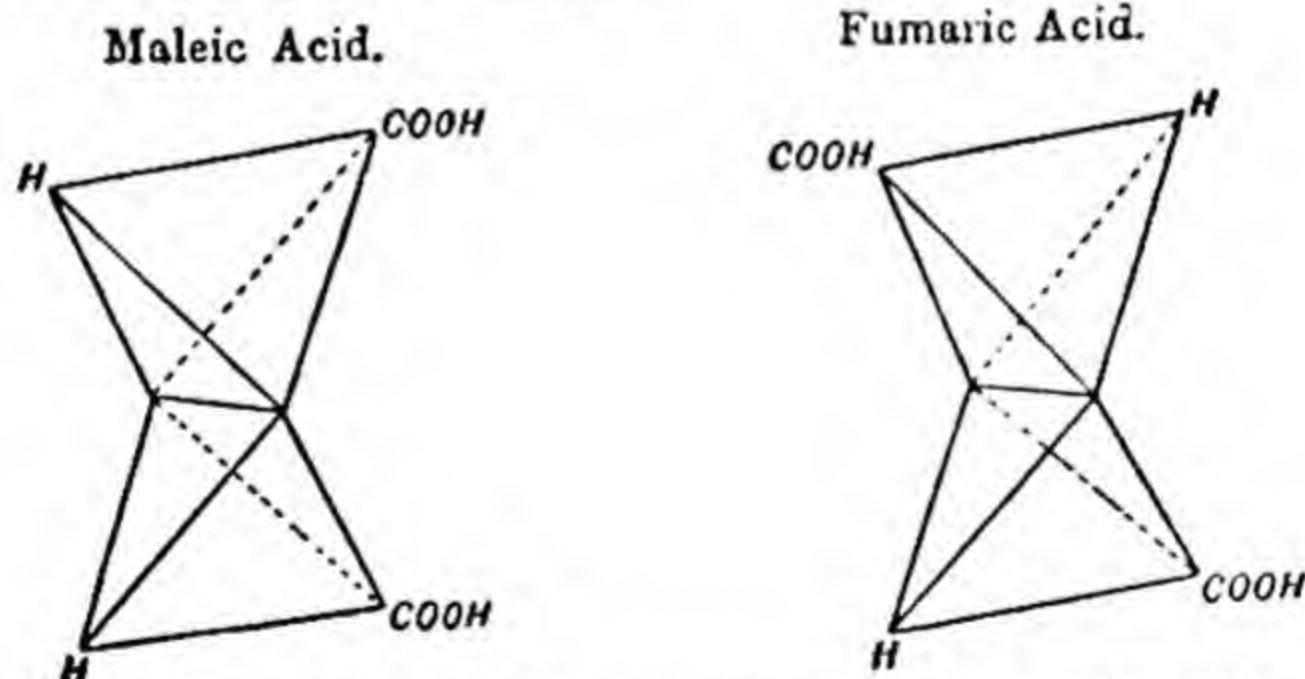


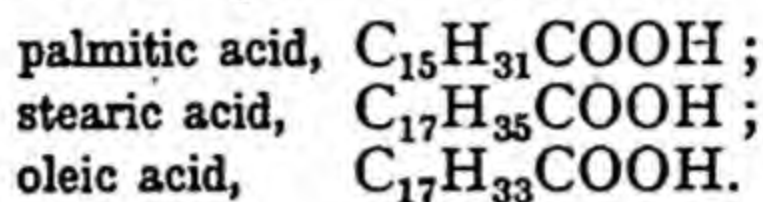
FIG. 331 —*Cis-trans*-ISOMERISM EXPLAINED ON THE TETRAHEDRAL THEORY.

IN THE *cis*-COMPOUND, MALEIC ACID, THE SIMILAR GROUPS (H AND COOH) ARE ADJACENT; IN THE *trans*-COMPOUND, FUMARIC ACID, THEY ARE OPPOSITE. THE TETRAHEDRA CANNOT ROTATE BECAUSE THEY ARE JOINED BY A DOUBLE BOND.

In this case the tetrahedra are joined along an edge, corresponding with the double bond. Whereas optical isomers (e.g., the

tartaric acids) are identical in chemical properties and in all physical properties (*e.g.*, solubility) except optical activity, *cis*- and *trans*- isomers differ in these properties.

**Oils and fats.**—Oils and fats contain glycerol esters of palmitic, oleic, and stearic acids. Glycerol is an alcohol containing three hydroxyl groups,  $C_3H_5(OH)_3$ ; the three fatty acids mentioned have rather complicated formulae :

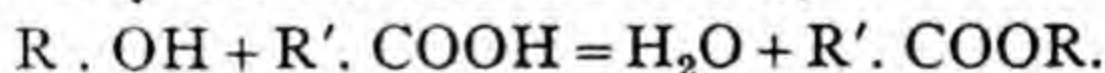


Butter fat contains also about 2 per cent. of the glycerol ester of butyric acid,  $C_3H_7COOH$ ; castor oil is the glycerol ester of ricinoleic acid.

*Margarine* (called *oleomargarine* in America) is a butter substitute made from a mixture of purified fats, churned with milk to a butter-like emulsion and generally coloured yellow. Beef fat, lard, olive oil, cottonseed oil, refined coconut oil and palm oil, and in America hardened cottonseed oil (p. 292), are all used.

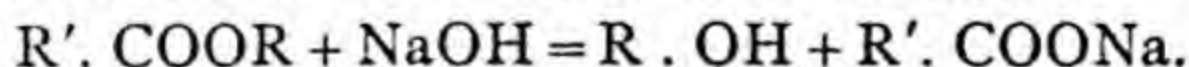
**Drying oils**, such as *linseed oil*, contain glycerides of unsaturated acids (containing double bonds in the molecules) which undergo oxidation on exposure to air, especially after being 'boiled,' and solidify. They are used for paints. (p. 279). *Linoleum* is a mixture of cork dust and mineral pigments ground up with oxidised linseed oil and applied to canvas. To increase the rate of 'drying' (*i.e.* oxidation) of the boiled linseed oil, *driers* are added: these are catalysts and contain lead and manganese salts.

**Soap.**—By the interaction of an acid with an alcohol, water is eliminated and an ester ('etheral salt') is formed (*e.g.*, ethyl acetate, from ethyl alcohol and acetic acid):



Many esters are used for flavouring, *e.g.*, amyl acetate.

When an ester is boiled with a solution of an alkali, the alcohol and an alkali salt of the acid are formed:

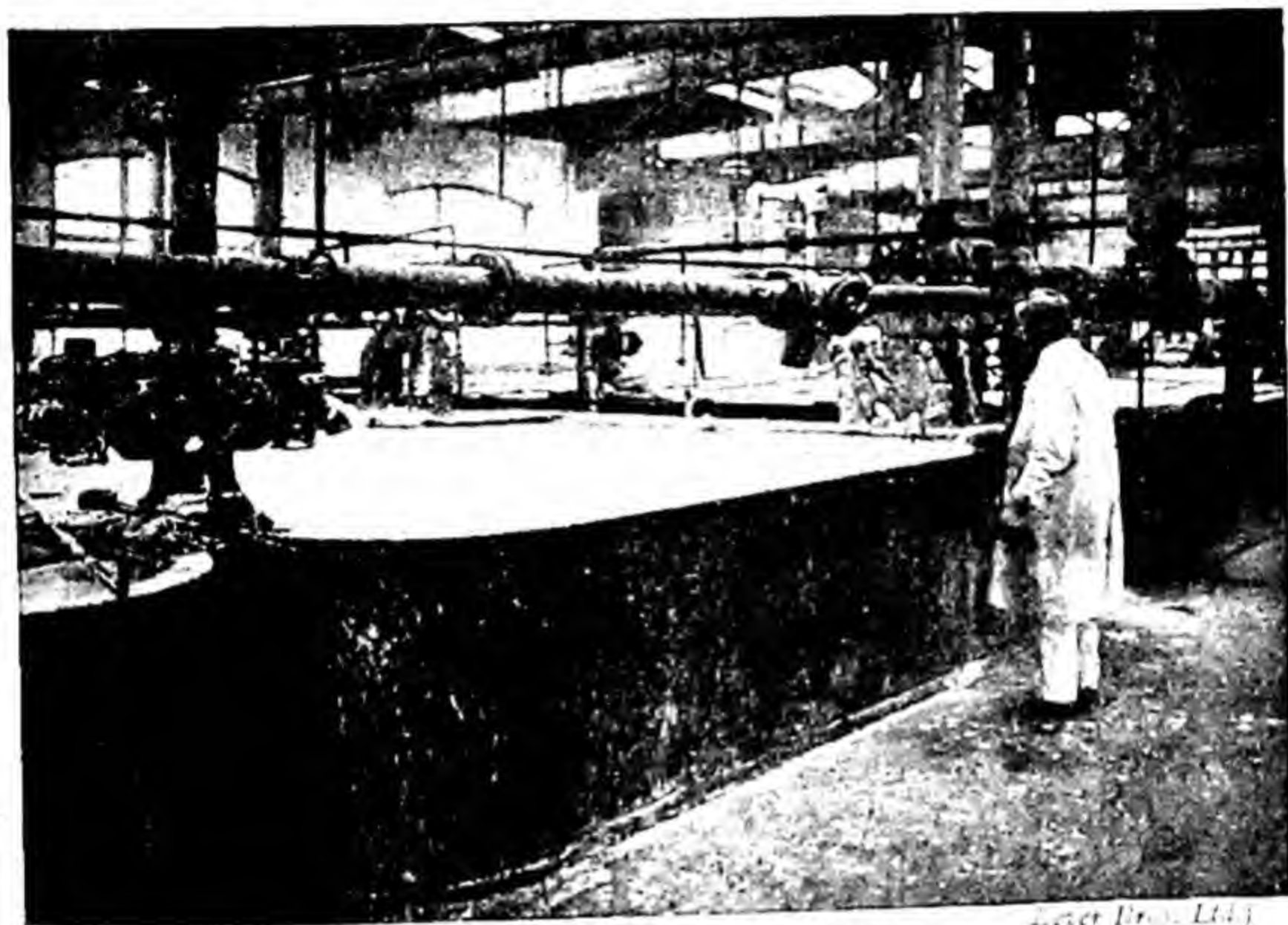


This process is called **saponification**.

The alkali salts of palmitic, oleic, and stearic acids are called soaps. They are made by boiling oils or fats (*e.g.*, olive oil, palm oil, tallow) with caustic soda solution, when a solution containing soap and glycerol is formed.



The soap 'curd' thrown out of the mixture by common salt is heated with water to form a paste, which is again boiled with a little caustic soda, again separated into two layers, and the process may be repeated. The soap is then 'fitted,' *i.e.*, brought into the state of finished soap, by allowing it to stand and taking



*Leet Bros. Ltd.*

FIG. 332.—A SOAP KETTLE.

THE FATS AND ALKALI ARE BOILED BY MEANS OF STEAM COILS IN THE PANS.

off the top layer, which is agitated in 'crutching' machines, after which it is allowed to solidify in soap frames and then cut into bars.

The residual liquor from which the soap curd separated contains the glycerol, which is obtained from it by distilling it under reduced pressure in a current of superheated steam.

During the Great War, Germany became very short of fats for making glycerol to be used for explosives and obtained it by fermenting molasses with yeast in presence of large quantities of sodium sulphite, when instead of the normal production of glycerol to the extent of about 3 per cent. of the sugar fermented, over 30 per cent. can be obtained.

When the fats or oils are saponified with caustic potash instead

of caustic soda, the potassium salts of the fatty acids, together with glycerol, result. The product is **soft soap**: it is allowed to set to a jelly and not thrown out with salt. The best kind of soft soap is made from linseed oil.

*Carbolic soap* contains phenol and other substances present in the middle oil of coal tar (p. 523), which is added during the boiling. In making *toilet soap*, the soap is cut into shreds, which are dried, milled by passing between heavy rollers, mixed with colour and perfume, and squeezed into bars by a powerful hydraulic press. The bars are cut into tablets, which are then stamped into oval or other shapes.

*Transparent soap* is produced by dissolving soap in alcohol and evaporating or (for the cheaper kinds) by adding glycerol or sugar to ordinary soap.

*Marine soaps* are so called because they are soluble in a solution of salt and hence can be used with sea water. Such soaps are usually made from coconut oil and may contain sodium sulphate, soluble silicates, fuller's earth, and starch.

**Washing with soap.**—The modern explanation of the detergent action of soap is very interesting. The molecules of a liquid exert great cohesive attractions on one another: every liquid, it has been calculated, is internally under a pressure of 800-3000 atm. owing to these forces. At the surface of the liquid, whether a free surface or a surface of contact with a solid, *e.g.*, the containing vessel, the molecules are pulled inwards and the surface is thus rather like a strongly stretched skin—stretched because the molecules in the surface pull one another sideways. The surface thus tends to shrink and become as small as possible.

The force acting in the surface in this way is called **surface tension**: it is not large, and varies rather considerably with the nature of the liquid. The surface tension is not usually much affected by dissolving salts or other substances in the liquid, but some particular materials lower the surface tension of water very considerably, *e.g.*, soap, gum, albumin (white of egg) and other colloidal materials (p. 176). Such solutions froth easily when shaken. One per cent. of soap will halve the surface tension of water. It is also known that when this happens, the molecules of the dissolved substance tend to accumulate at the surface of the solution, and to arrange themselves in the surface vertically side by side, with their 'heads' all facing in one direction and their 'tails' in the opposite direction. The arrangement of molecules at surfaces in this way, to form films, which are generally one molecule thick, and with the molecules



orientated, is called **adsorption**. Adsorption also occurs with gases on solids, such as charcoal (p. 409)

In unimolecular films of fatty acids on water the carboxyl group at one end of the chain has an attraction for water and is immersed in it; the hydrocarbon radical at the other end of the chain, which resembles paraffin oil in showing no tendency to wet itself, projects vertically from the film.

Soap, since it lowers the surface tension of water, is adsorbed in the surface film, and if a solid is present it is adsorbed by it. When a solution of soap is shaken with kieselguhr (p. 470) it adheres to the fine powder and is removed from the solution. When a large amount of soap solution is brought in contact with 'dirt,' the fine solid particles are, as it were, adsorbed by the soap and pass into the liquid. Oil and grease are also broken up or emulsified by the soap solution, and removed.

**Candles ; wax.**—Materials used in making candles are tallow (now only 'used for miners' candles), paraffin wax (p. 435), beeswax (used mainly for church candles) and stearin.

When fats are treated with superheated steam in the presence of a little slaked lime, they are hydrolysed into glycerol and free fatty acids. The glycerol is separated for purification and the fatty acids distilled. The liquid oleic acid is separated by the application of great pressure, and the resulting solid mixture of fatty acids, principally stearic acid, with some palmitic acid, is called **stearin** and is used for making candles, after the addition of a small quantity of paraffin wax. Stearin candles do not soften and bend in warm weather, as do paraffin candles. In another process the hydrolysis of the fat is carried out by heating with water and *Twitchell's reagent*, made by heating castor oil, or oleic acid and naphthalene, with sulphuric acid.

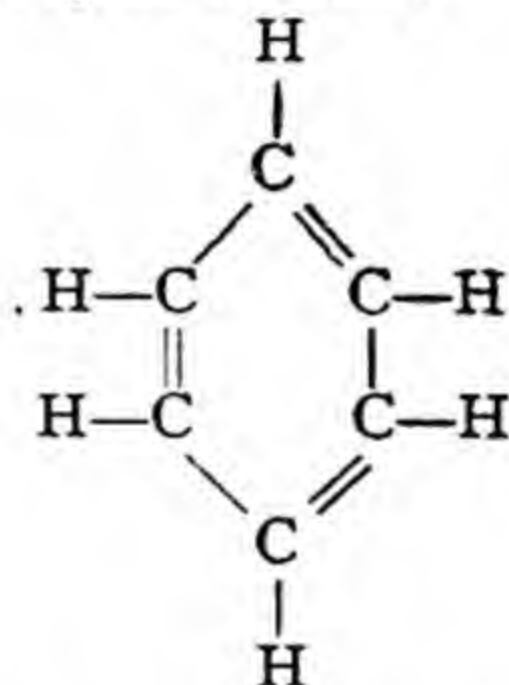
Waxes are not glycerides. **Beeswax** consists of a free organic acid called cerotic acid, together with the palmitic ester of myricyl alcohol,  $C_{30}H_{61}OH$ , the latter taking the place of the glycerol in ordinary fats. **Spermaceti** is a wax obtained from the oil of the sperm whale, and in China and Japan large quantities of *tree wax* are used for candles, this material being formed by a small crustacean like a wood louse. Various vegetable waxes are also used.


## CHAPTER XXVIII

### ORGANIC COMPOUNDS (*Continued*)

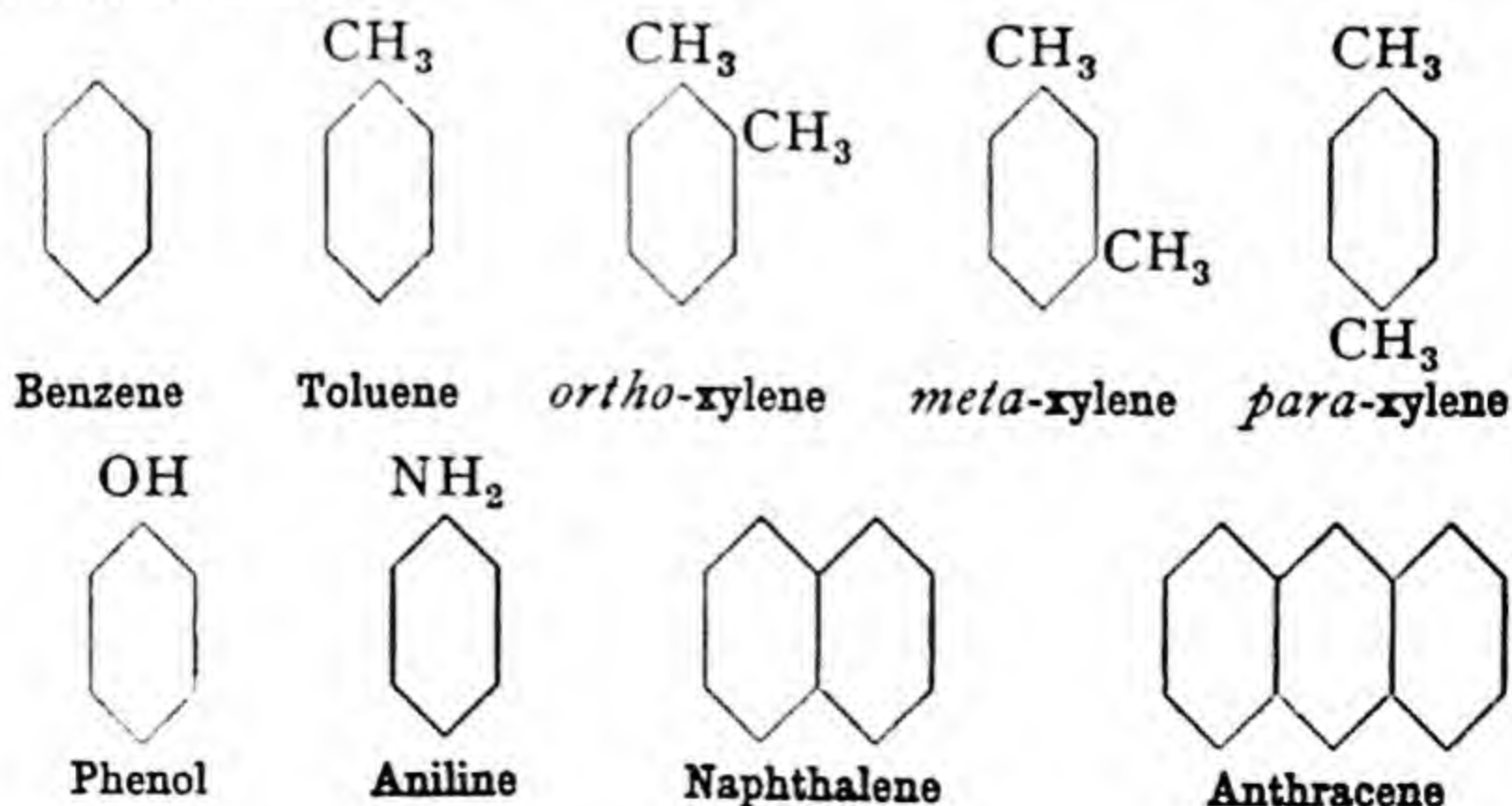
**Aromatic compounds.**—The compounds described in the last chapter are **aliphatic** (fatty) or **open chain** (p. 432) compounds: those now to be considered are mainly **aromatic**, containing closed *rings* of carbon atoms. The raw material for the production of aromatic compounds is chiefly coal tar.

The simplest aromatic compound to be considered is **benzene**, the formula of which may be written :



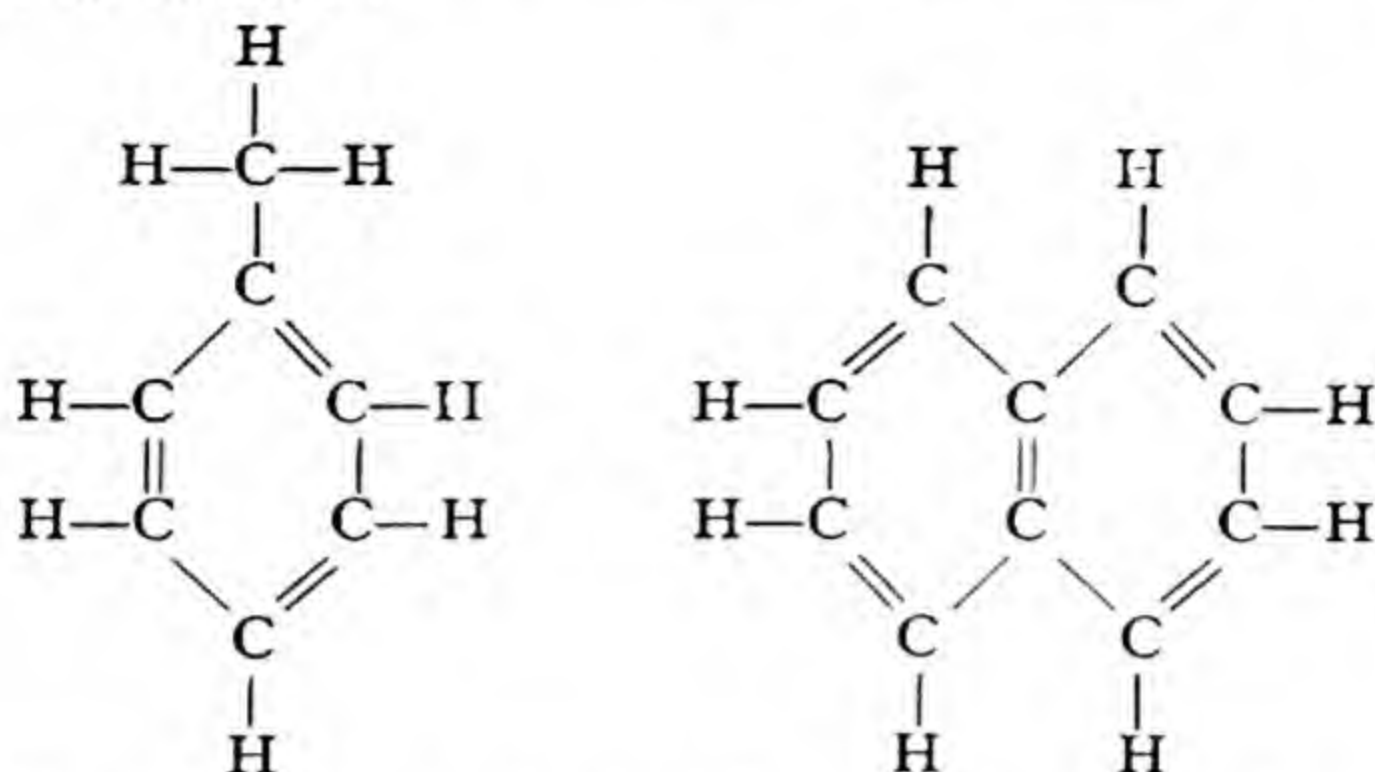
but is usually denoted by a simple hexagon: . When

atoms of hydrogen are substituted by other atoms or radicals, the products are denoted by the hexagon formula with the substituting group or atom written opposite the position where it is attached :





The formulae of toluene and naphthalene, for example, written in full are :



**Coal tar.**—This is a mixture of a great number of materials, chiefly hydrocarbons, obtained in the distillation of coal (p. 444). It is separated by distillation into a number of fractions. A *light oil* contains benzene, toluene, and xylenes (p. 522); *creosote* contains phenol (carbolic acid) and *cresols* (dihydroxybenzenes), which are antiseptics, and is used in preserving timber; the *heavier fractions* contain more complicated aromatic hydrocarbons, such as naphthalene and anthracene, which when purified are solids and are used in the manufacture of dyes. The residue in the retort is *pitch*, used for road-making. Four fractions are generally collected in the distillation, viz. *light oil*, *middle oil*, *heavy oil*, and *anthracene oil*. The *middle oil* contains most of the phenol and the naphthalene; the *heavy oil* begins to come over when the temperature reaches about  $270^{\circ}$ ; it contains cresols and naphthalene; *anthracene oil* comes over from about  $275^{\circ}$ , and the distillation is stopped when the pitch residue has the required consistency. The amounts of the fractions are, approximately, as follows :

	Temperature	Specific gravity	Percentage recovered
Water - -			4-5
Light oil - -	$170^{\circ}$ - $180^{\circ}$	0.91-0.95	2-4
Middle oil - -	$240^{\circ}$ - $245^{\circ}$	1.01-1.02	10-12
Heavy oil - -	$270^{\circ}$ - $275^{\circ}$	1.04	8-10
Anthracene oil - -	$300^{\circ}$ - $340^{\circ}$	1.09	18-25
Pitch - -	—	1.3	50-60

A method of continuous distillation is also used, in which superheated steam is blown into the tar, previously heated to about  $300^{\circ}$  under pressure.

The various products of the distillation of tar are further worked up and purified by methods which cannot be described here.

The so-called 'coal-tar dyes' are not, of course, contained as such in the tar. They are prepared by chemical processes from the constituents of the tar, *e.g.*, the benzene is first converted into aniline, and the aniline then treated to produce dyes. Some dyes are made from naphthalene and some from anthracene. When purified naphthalene is heated under pressure with hydrogen in presence of a nickel salt, one of the benzene rings takes up four atoms of hydrogen and a liquid called **tetralin** is formed, used as a solvent, and in Germany as a motor fuel when mixed with alcohol and benzene.

**Explosives.**—Explosives are solid, liquid, or gaseous compounds or mixtures which by chemical action, initiated by flame, percussion, or the detonation of other explosives, generate suddenly large volumes of heated gas. In some cases the method of firing influences the effect: guncotton when lit with a match burns fiercely but does not explode, but when exposed to the shock of detonating mercury fulminate it explodes violently.

The chief uses of explosives in peace are in getting coal and other minerals and in blasting or removing rock, roots of trees, etc. The oldest explosive is **gunpowder**, which is an intimate mixture of potassium nitrate (six parts) with charcoal (one part) and sulphur (one part), ground and incorporated under stone rollers.

Gunpowder was apparently first used by the Chinese for fire-works and military purposes about A.D. 1150, if not earlier. *Greek fire*, used in Europe in the Byzantine period, was apparently a mixture of resin, pitch, salt, sulphur, and quicklime, which could ignite in contact with water: some kinds *may* have contained saltpetre. The invention of gunpowder in the West is usually ascribed to the English Franciscan monk, Roger Bacon (1214-1292), who in his *de secretis operibus artis et de nullitate magia*, probably composed about 1248, definitely mentions saltpetre and sulphur as constituents, but is supposed to conceal charcoal in an anagram (see Fig. 333). The full recipe is given in the *Liber Ignium* of Marcus Graecus, the earliest MSS. of which are practically contemporary with Bacon, and also give recipes for 'liquid fire' for military purposes. Gunpowder was first used by the English in the battle of Crecy, in 1346.

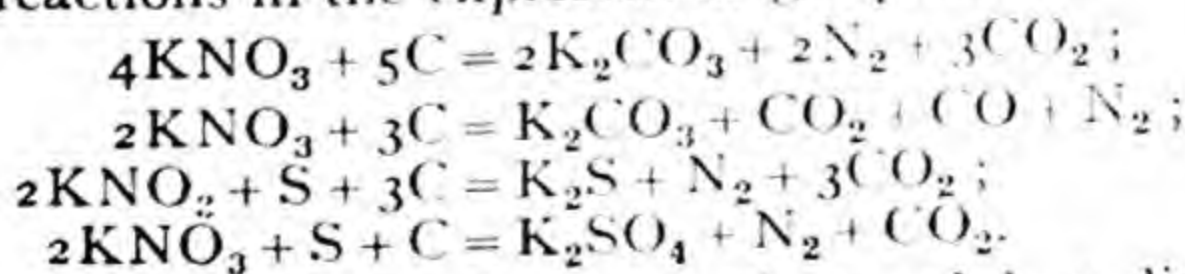


The explosion of gunpowder is a very complicated chemical reaction and cannot correctly be represented by any single chemical equation. The gaseous product consists principally of carbon dioxide, carbon monoxide, and nitrogen, whilst the solid product (including that in the dense smoke) consists



FIG. 333.—PAGE OF BACON MS. WITH DESCRIPTION OF GUNPOWDER.  
(British Museum.)

mainly of potassium carbonate, potassium sulphate, and potassium sulphide. We may thus consider the following as the principal reactions in the explosion of gunpowder:



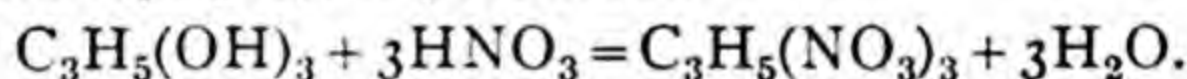
In the action of sulphur alone on nitre, sulphur dioxide and potassium nitrite are also formed as well as potassium sulphate.

For many purposes gunpowder has been replaced by modern explosives, such as *cordite* and *dynamite* (*q.v.*), but it is still used in coal mines for breaking up the large masses of coal.



FIG. 334.—DYNAMITE CARTRIDGES IN BORE HOLE WITH DETONATOR AND FUSE FOR INITIATING THE EXPLOSION.  
(Nobel's Explosives Co.)

By treating glycerol with a mixture of concentrated nitric and sulphuric acids, the nitric acid ester, *nitroglycerin*, really glyceryl nitrate (p. 518), is produced :



It was discovered by Sobrero in 1846 but was first used as an explosive by Nobel in 1862. It is an oily liquid which detonates

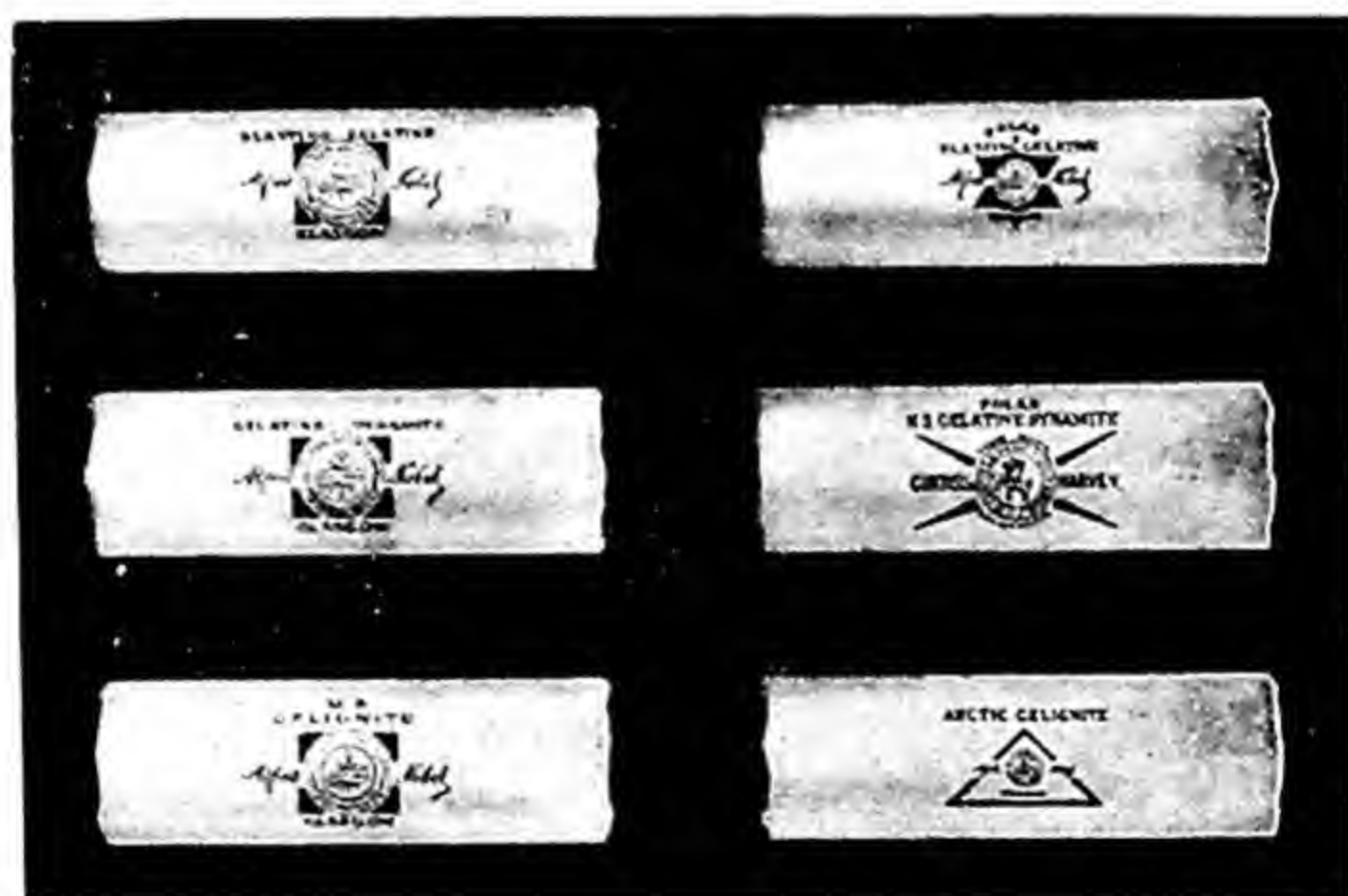


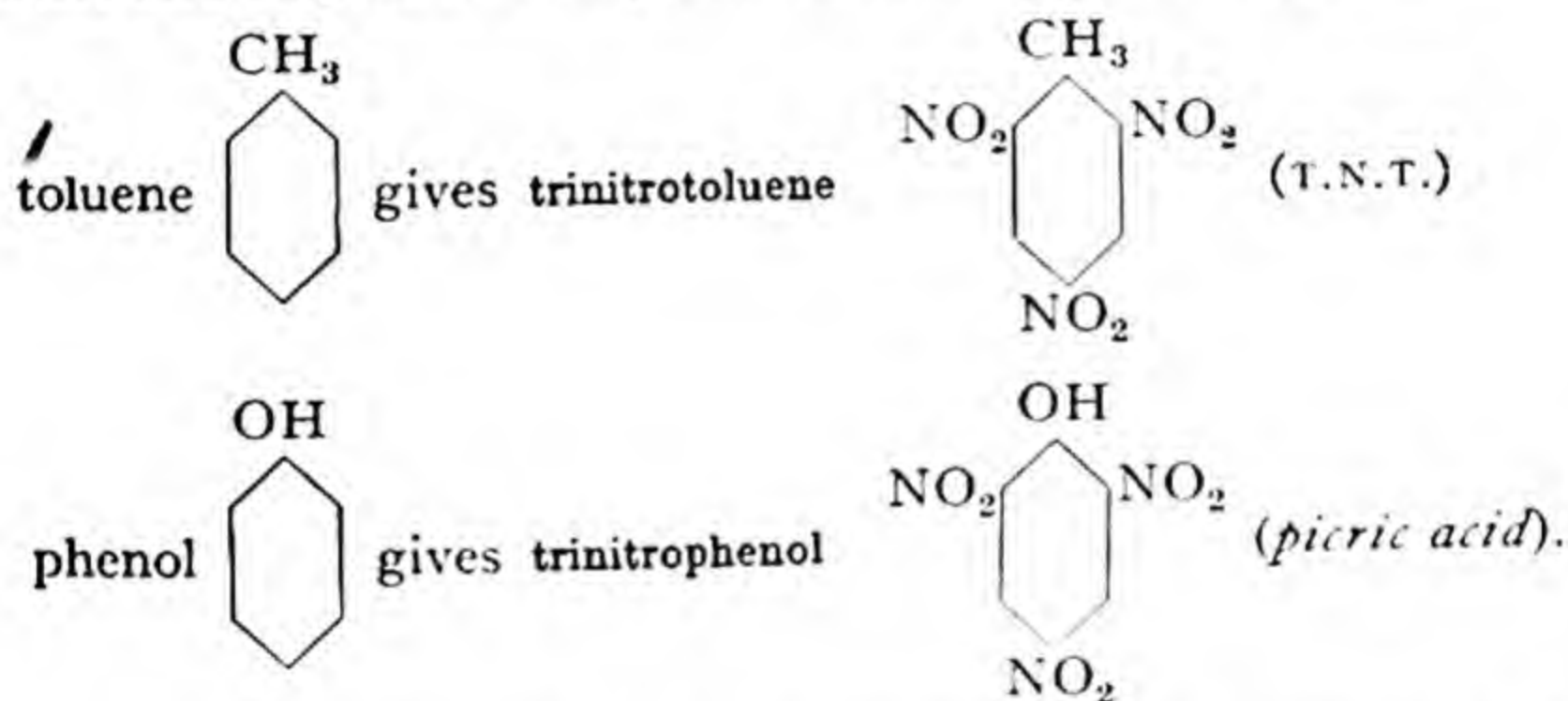
FIG. 335.—DYNAMITE AND BLASTING GELATINE CARTRIDGES.  
(Nobel's Explosives Ltd.)

with terrible violence when struck and is too dangerous to use as such. Nobel showed that it can be soaked up in a porous earth, *kieselguhr*, to form *dynamite*, which is safer. Dynamite is now mostly produced by mixing nitroglycerin with wood



powder together with mineral nitrates. It detonates with tremendous violence when exposed to the shock of exploding mercury fulminate. Another useful explosive is *guncotton*, discovered by Schönbein in 1845: it is a nitrocellulose (p. 499) obtained by the action of a mixture of concentrated nitric and sulphuric acids on cotton. Guncotton detonates violently, even when wet, on exposure to the shock of exploding mercury fulminate. **Blasting gelatine** and **gelignite** are composed of nitroglycerin and guncotton: they also detonate with mercury fulminate.

Important explosives are produced by substituting hydrogen in aromatic compounds by the nitro-group,  $-\text{NO}_2$ ; they are generally obtained by treating the substances with concentrated nitric and sulphuric acids, and the following are important:



T.N.T. and picric acid (*lyddite*) are 'high explosives' used for filling shells. On the explosion of T.N.T. alone, large volumes of black smoke are evolved, so that shells filled with it were nicknamed 'Jack Johnsons' (after a negro pugilist) in the Great War. It was found that a mixture of T.N.T. with four times its weight of ammonium nitrate (which is itself an explosive), called **amatol**, was a more effective and cheaper explosive, and this was extensively used. On account of the addition of the oxidising agent (ammonium nitrate) the formation of black smoke was avoided.

The explosives used in getting coal in mines must not be too violent, as otherwise the coal would be shattered to dust. They must also not give a hot flame, which might ignite fire-damp (p. 449). *Safety explosives* are therefore used (sometimes called 'permitted explosives'): they include various mixed explosives,

such as dynamite with salts (Glauber's salt, etc.), ammonium nitrate and hydrocarbons, etc. Gunpowder, although used in mines, is not a safety explosive.

Explosives such as dynamite, T.N.T., amatol and picric acid burn with extreme rapidity on detonation and exert a great shattering effect. They are called **brisant explosives**: those suitable for filling shells, such as T.N.T., amatol, and picric acid, are generally called **high explosives**. They are quite unsuitable

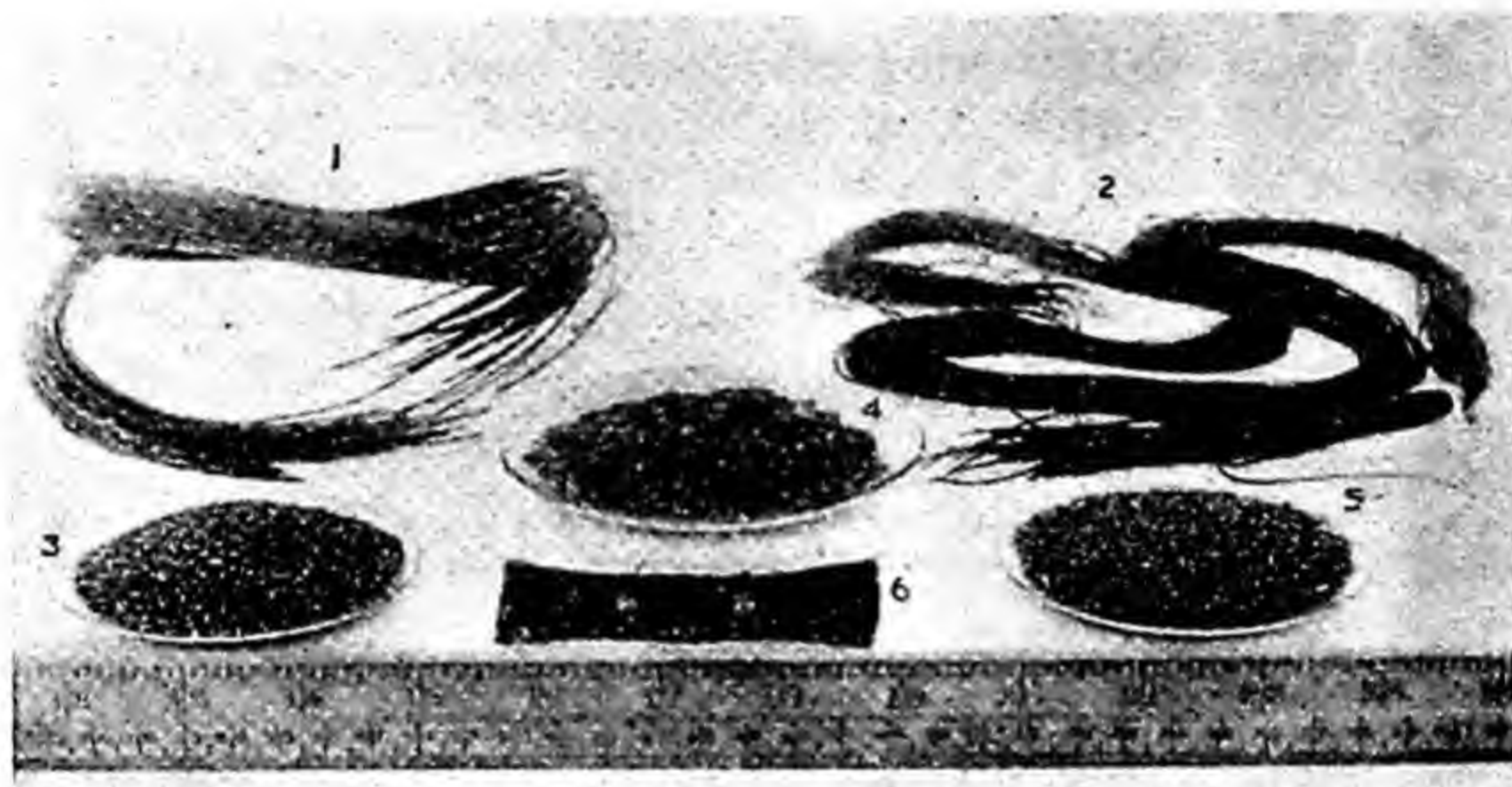


FIG. 336.—VARIETIES OF CORDITE AND SMOKELESS POWDERS.

- (1) CORDITE M.D. TUBULAR SIZE  $5\frac{1}{2}$  FOR .303 Mk. VII SERVICE RIFLE.
- (2) CORDITE M.K.I. SIZE  $3\frac{1}{4}$  FOR .303 Mk. VI SERVICE RIFLE.
- (3) TUBULAR NITROCELLULOSE RIFLE POWDER.
- (4) CORDITE M.K.I. SIZE 20 S.C. FOR BLANK AMMUNITION.
- (5) FLAKE NITROCELLULOSE RIFLE POWDER.
- (6) CORDITE M.D. SIZE  $4\frac{1}{2}$  FOR HOWITZERS.

(Nobel's Explosives Co.)

for use in guns, since the pressure would be developed so suddenly that the gun would burst. Another kind of explosive is required for this purpose, called a **propellant**. Gunpowder and cordite are propellants. Cordite is made by gelatinising gun-cotton with nitroglycerin and a little castor oil or vaseline. The gelatinous mass is pressed into threads, tubes or tablets, and is largely used as a 'smokeless powder.' The cordite is made up in various forms for special purposes (Figs. 336 and 337).

The tremendous power of modern explosives may be realised from the fact that a modern gun will fire a projectile weighing nearly a ton over a distance of thirty miles. When we take into account the very short interval of time during which the shell is



in the gun during the explosion, the 'horse-power,' or rate of doing work, is seen to be very high.

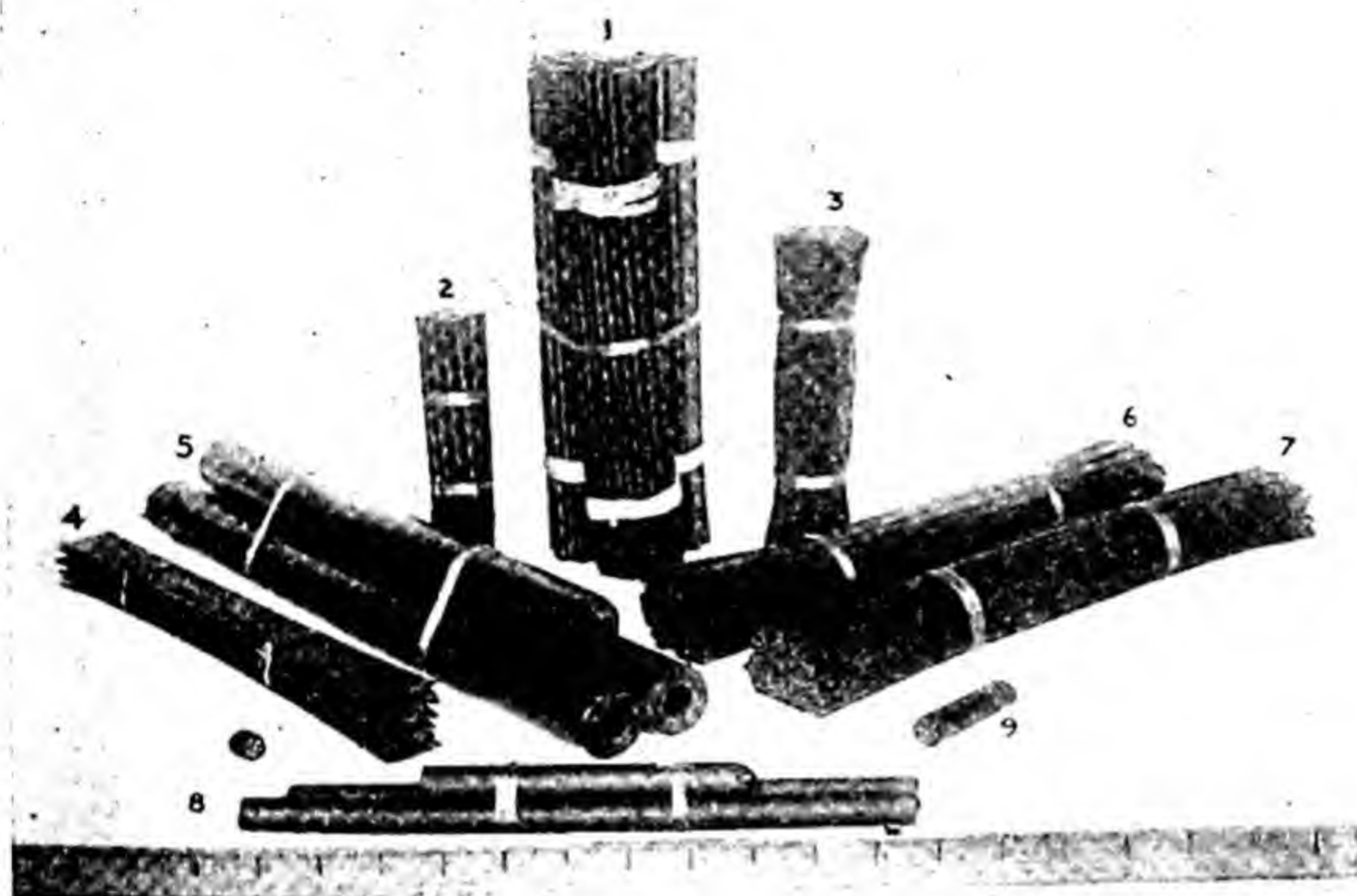


FIG. 337.—VARIOUS FORMS OF CORDITE IN RODS AND STRIPS.

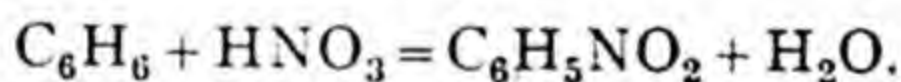
- (1) CORDITE M.D. TUBULAR.
- (2) CHILWORTH SMOKELESS POWDER NO. 2 OR NACOTA POWDER.
- (3) CORDITE M.D. SIZE 10.
- (4) NITROCELLULOSE STRIP ORDNANCE POWDER.
- (5) NON-SOLVENT CORDITE FOR HEAVY ORDNANCE.
- (6) NITROCELLULOSE FLAKE ORDNANCE POWDER.
- (7) NON-SOLVENT CORDITE FOR FIELD ARTILLERY.
- (8) CHILWORTH SMOKELESS POWDER NO. 2.
- (9) NITROCELLULOSE MULTITUBULAR ORDNANCE POWDER.

(Nobel's Explosives Co.)

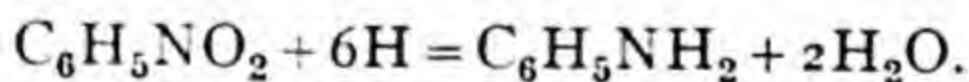
**Dyes and dyeing.**—It has been explained that in the early period the materials used in dyeing were of vegetable origin, with the exception of the Tyrian purple (obtained from shell-fish) and the red dye obtained from the kermes insect. Indigo and madder are examples of vegetable dyes. Many new dyes were rendered available with the discovery of America, among them logwood and cochineal. About 1650 a great improvement in dyeing took place by the substitution of a tin salt for alum as a mordant (p. 531), and with cochineal a very brilliant scarlet was so produced. The invention is attributed to Cornelius

Drebbel (who constructed a submarine in 1622) in 1630, and his son-in-law established a large dye-works at Bow. There was much prejudice against logwood and indigo during the sixteenth century, and the cultivators of woad arranged that the foreign dyes should be prohibited in England under heavy penalties. Until the reign of Charles II. any indigo and logwood found in the country were confiscated and burnt. Calico printing was not much practised in Europe until about 1700, in which year the importation of printed chintzes from India to England was forbidden. This was followed by a law enacted in 1720 which prohibited the wearing of all printed calicos whatever, whether imported or home produced. In this case the interests of the silk, wool, and linen industries were the underlying cause, and it was not until 1831 that all restrictions were removed.

The year 1856 marks a turning point in the dye industry, for it was then that William Perkin, whilst a young student, discovered the first aniline dye, *mauve*, when trying to make quinine. Another dye discovered soon after was *magenta*. The starting material for these dyes was *aniline*, a derivative of benzene, in which an atom of hydrogen is replaced by the amino-group,  $-NH_2$  (p. 522). Aniline is a liquid first obtained by Unverdorben in 1826 by the distillation of indigo but made from benzene by Zinin in 1846 by the following process. Benzene is converted into nitrobenzene by treatment with nitric and sulphuric acids ('nitration'):



The nitrobenzene is then reduced to aniline by iron filings and hydrochloric acid:



Perkin's mauve was obtained by the action of potassium dichromate on aniline. It is a rather fugitive colour.

The synthetic dye industry was developed on a small scale in England and on a vast scale in Germany. Since the Great War synthetic dyes have been made on a large scale in England and in the United States of America.

The *colour* of a dyestuff is very closely related to the way in which the atoms in the molecule are linked together, and the presence of certain groupings of atoms. By introducing such groups new shades and colours may often be produced.



Not all coloured substances are dyes. In order to constitute a dyestuff, as distinguished from a coloured substance, a substance must be strongly coloured in itself, or produce coloured bodies with a mordant; it must be capable of being fixed upon the textile from an aqueous solution; and it must produce a colour sufficiently resistant to washing with soap and exposure to air and light. Some dyes may be used directly by merely soaking



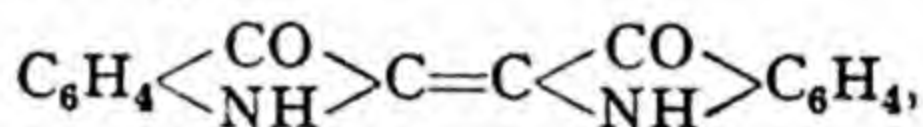
FIG. 338.—INTERIOR OF A DYEWORKS.  
(Bradford Dyers' Assoc. 1211)

the fabric in a solution of the colour, and are called substantive, or **direct, dyes**. Others require the use of other substances, generally metallic salts, called mordants, and are called adjective, or **mordant, dyes**. Mordants are usually salts of aluminium, chromium, iron, or tin, the colloidal hydrated oxides of which, produced by hydrolysis when the tissue (generally wool) is heated in a solution of the salt, are deposited on the fibres and serve to attract the dye from a solution, and to bind it firmly to the tissue. In the case of cotton, the textile is first treated with an

antimony salt and tannin, which form a precipitate on the fibres, or with solutions of salts of metals with very weak acids such as acetic acid, which are decomposed by heat, depositing the hydrated oxide on the fabric. In another process the fabric is first soaked in a solution of a metallic salt and then in an alkaline hydroxide, when the hydrated metallic oxide is deposited. Some synthetic dyes can be used with cotton without a mordant, and many dyes can be used directly with wool and silk. Tannic acid alone is used on cotton with basic dyes.

Indigo is what is called a *vat-dye*. A solution of indigo-white is prepared by reducing the indigo. The wool is steeped in this and exposed to air, when indigo blue is produced by oxidation and is deposited in the body of the fibre. The plant woad, used by early Keltic tribes, was similarly applied and yields indigo blue.

The formula of *indigotin*, one of the principal constituents of indigo, is rather complicated :



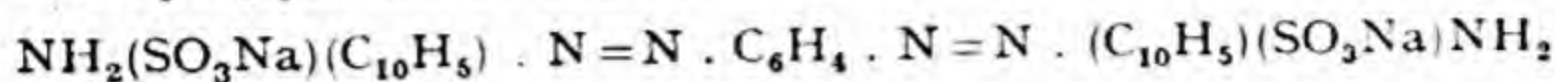
but it gave an unmistakable clue to the manufacture of the dye. Indigotin is now very largely made artificially : in one important process, naphthalene and ammonia from coal, acetic acid from wood (or calcium carbide, see p. 442), and oxygen from the air are the principal raw materials : sulphuric acid, chlorine, mercury, and alkali are also used in the various steps of the process, but are recovered. The long series of experiments leading to this discovery cost the German firm, it is said, a million pounds.

The first step in this process is to convert naphthalene into phthalic acid, a process which occurs when it is heated with concentrated sulphuric acid, but too slowly to be technically utilisable. One day, in the laboratory, it is said, a thermometer bulb broke in the mixture, and the process then went on rapidly. Mercury is a catalyst for the reaction. Some careless chemist or laboratory assistant, therefore, laid the foundation of the indigotin industry, and we are left to wonder whether another million pounds would have been spent without success but for this unknown Faraday. These 'romances of chemical industry,' it may be added, are often fictitious. As often as not the 'discoveries' come from forgotten patent specifications, or publications in pure science. The valuable medicinal properties of acetanilide were, it is true, discovered because this material



had been supplied by mistake instead of naphthalene by a laboratory boy.

Although the formula of indigo blue appears complicated, it is completely overshadowed by those of other dyes. *Congo red*, for example, possesses the formula :



and there are many dyes with much more complex formulae than this. In the Congo red molecule the colour-producing group, called a **chromophore**, is the doubly-linked nitrogen  $-\text{N}=\text{N}-$ ; when in addition to a chromophore the molecule contains a basic group, such as  $-\text{NH}_2$ , or an acidic group, such as  $-\text{OH}$  or  $-\text{SO}_3\text{H}$ , a dyestuff is formed. The chromophore in indigotin is



A type of molecular structure producing colour in benzene derivatives, or other compounds containing benzene rings, is the **quinonoid grouping** :



Many dyes when reduced yield colourless **leuco-compounds**, which produce the dyes on oxidation. Indigo-white is a leuco-compound.

Another important dyestuff is alizarin, formerly obtained from the madder root and used to dye cotton *Turkey red*. This is now obtained, not from aniline, but from the hydrocarbon **anthracene**,  $\text{C}_{14}\text{H}_{10}$ , obtained from coal tar (p. 523). By oxidation this yields **anthraquinone**,  $\text{C}_{14}\text{H}_8\text{O}_2$ , and by substituting two atoms of hydrogen in this by hydroxyl groups one obtains **dihydroxyanthraquinone**,  $\text{C}_{14}\text{H}_6\text{O}_2(\text{OH})_2$ : this substance is alizarin. Whereas 50,000 acres were devoted to the cultivation of madder in France alone, none is now grown, although the production of alizarin has risen from 750 tons in 1870 to 2000 tons per annum.

**Essential oils.**—Many plants, especially varieties of *Coniferae* and *Citrus*, contain volatile substances with powerful odours, sparingly miscible with water, and hence grouped together under the name of **essential oils**. Some of these are esters (p. 518; e.g., oil of wintergreen; pear essence; lavender oil; quince oil), some are aldehydes (e.g., oil of bitter almonds or benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ ; citral; cumin oil), some are hydro-

carbons (oil of turpentine ; dill oil), some are alcohols (menthol), some are ketones related to acetone (camphor), and some are phenols related to phenol (oil of cloves). They may be prepared by distilling the plant, or the part of the plant rich in the essential oil (*e.g.*, lemon peel, cloves, cinnamon) in a current of steam, when they pass over. They are only slightly soluble in water, but impart a strong odour and taste to it. Oil of turpentine is prepared by distilling an exudation from pines and other coniferous trees. Common rosin (or resin) remains in the still.

The chief constituent of oil of turpentine is the hydrocarbon pinene, with the formula  $C_{10}H_{16}$ . Limonene is another terpene, or hydrocarbon related to turpentine, found in lemon rind and giving it its characteristic odour. Camphor has the formula  $C_{10}H_{16}O$ , and is obtained by the steam distillation of the roots and trunks of a tree growing in China, Formosa, and Japan : it is only very sparingly soluble in water but readily soluble in alcohol, forming 'spirit of camphor.' Eucalyptus oil consists mainly of cineol,  $C_{10}H_{18}O$  ; thymol, a phenol (*cf.* p. 523), is an antiseptic contained in oil of thyme, and eugenol, another phenol, is contained in oil of cloves.

**Rubber** (*caoutchouc*).—This valuable material is a polymerised form of the liquid hydrocarbon isoprene,  $C_5H_8$ , which is formed on distilling rubber. Isoprene may also be obtained from acetone and in other ways, so that many attempts have been made to obtain synthetic rubber. So far, the products made artificially are more expensive than natural rubber, but some of them have valuable properties, *e.g.*, they are more resistant to oil than natural rubber. One such product on the market is *chloroprene*, which contains combined chlorine.

Natural rubber is formed by the coagulation of the milky juice (*latex*) of various tropical and sub-tropical trees of different families, but particularly the *Hevea* in many varieties. The latex is obtained by 'tapping' (making incisions in the stem) and is then coagulated. The coagulation is effected by repeatedly dipping a paddle in the latex and holding it in the dense smoke from a brazier, forming *Para grades*, or in plantations by adding acetic acid to the colloidal latex, filtering off the coagulum, pressing it between rolls, and hanging up the sheets to dry, so as to form the *plantation grades*, smoked sheet and crêpe.

In the untreated state the elasticity of raw caoutchouc is imperfect, and ordinary rubber is obtained from it by **vulcanisa-**



tion. In this process it is heated with sulphur, a method discovered by Goodyear in America in 1839. Another process, invented by Parkes in 1843, called *cold vulcanisation*, consists in exposing thin sheets of raw rubber for a short time to a solution of sulphur chloride ( $S_2Cl_2$ ) in carbon disulphide, or exposing them to the vapour of sulphur chloride, and a third process introduced by Peachey in 1919 consists in subjecting the raw



FIG. 339.—A GIANT BRITISH AEROPLANE TYRE.

rubber to the combined action of hydrogen sulphide and sulphur dioxide, which liberate sulphur. Goodyear's hot vulcanisation process is mostly used, about 5 parts of sulphur being added to 95 of raw rubber and the mixture heated by steam under pressure. Some of the sulphur enters into combination with the rubber and the compound is adsorbed by the rest of the rubber. *Accelerators*, such as magnesia, litharge, and lime, and organic bases, such as aniline, etc., are also added to increase the rate of vulcanisation, and *fillers*, such as zinc oxide and gas carbon black (p. 410), are added to rubber made into motor tyres, as

they increase its resistance to abrasion. Red antimony sulphide is present in red vulcanised rubber. *Reclaimed rubber* is obtained by boiling finely divided waste rubber with alkali, and washing. Most of the world's supply of rubber is grown in the British Empire.

*Gutta-percha* and *balata* are (like rubber) originally milky exudations from trees, and are similar in composition to rubber. *Shellac*, which is more complex, is an excretion from the lac-insect living on an Indian tree, and is used in making sealing-wax and in solution in alcohol as a varnish, and for French polish. *Oleo-resins* are mixtures of resins and essential oils (*e.g.*, turpentine resin; copaiba balsam or Canada balsam); *gum-resins* (*e.g.*, myrrh) are natural mixtures of gums and resins.

By the dry distillation of rosin, a volatile *rosin spirit* is obtained, used as a substitute for turpentine (petrol is also used for similar purposes).

**Tannin; leather; ink.**—The name tannin is applied to a number of constituents of certain plants and trees which are amorphous, very soluble in water, have a bitter astringent taste, and possess two important properties made use of technically. First, they convert hides into leather, and second, they give with iron salts dark-coloured solutions called ink.

Nut-galls, which are excrescences on oaks produced by the puncture of the leaves and young twigs by an insect, are very rich in tannin, but the latter also occurs in oak and hemlock barks and in numerous other vegetable products used in tanning.

In making leather the hair is first removed from the hides by soaking in milk of lime, to which sodium sulphide may be added. The lime is removed from the skin by soaking in dilute acetic acid, sour bran (containing acetic and lactic acids), dung or dung substitutes (containing bacteria or trypsin, p. 552). The skin is then immersed in the tanning liquor containing the tannin, in pits. In the old process a long soaking in weak liquors was used; a more rapid process involves the use of stronger liquors but the product is said to be inferior. The tanned hide is then dried and treated with oil and tallow. Leather is coloured black by treatment with iron salts.

Mineral tanning replaces tannin by solutions of chromium salts: the process is rapid and the leather has a green colour. Thin leathers (*glacé* and *kid*) are tanned with alum. Chrome leather may be dried and impregnated with paraffin wax ('dripped'). *Artificial tannin* is made from formaldehyde and



substances formed by heating phenol ('carbolic acid') with sulphuric acid.

*Chamois leather* is not tanned, but the skin is rubbed with oil and this allowed to oxidise in the air. The oil is decomposed and the fatty acids are oxidised and combine with the skin. Such leather may be washed with soap and no oil can be extracted from it.

Ordinary ink is made from ferrous sulphate, tannin (or sometimes gallic acid, from the hydrolysis of the tannin in galls), and gum. This solution, containing ferrous tannate, has a very pale colour, so that a solution of indigo-sulphuric acid, or a blue dye is added. On exposure to air, the ferrous tannate is oxidised to ferric tannate, which has an intense black colour, and the blue colour of the ink gradually changes to deep black.

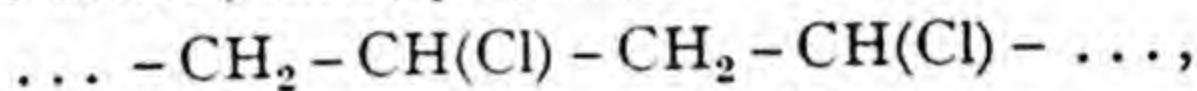
Such ink is first described by Isidore of Seville in 624 A.D. The earliest ink used in Egypt several thousand years ago was a carbon ink, made from finely-divided carbon (soot; lampblack) and gum. This is called 'Indian ink' or 'Chinese ink'; it is described by Vitruvius (24 B.C.) as *atramentum indicum* and was expensive, and the ordinary Roman ink was (as Dioskurides says) made from soot, gum, glue, and 'vitriol' (impure ferrous sulphate). Printers' ink is lampblack in boiled linseed oil; marking ink generally contains silver compounds which are reduced to an indelible black stain of silver.

**Alkaloids.**—The alkaloids are basic substances (hence the name) contained in plants, mostly dicotyledons, and many of them are the active principles of vegetable drugs. They probably play no useful part in the plant and are waste products. They all contain carbon, hydrogen and nitrogen, and also oxygen, except four liquid alkaloids, one of which is **nicotine**, the alkaloid of tobacco, which are free from oxygen. Their formulae are generally rather complicated.

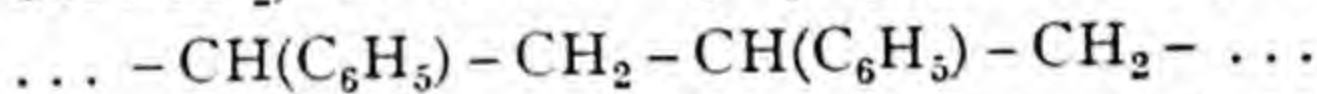
Important alkaloids are **theobromine**, of which cocoanibs contain 1.5–2.3 per cent.; **caffeine**, which is the alkaloid both of tea and coffee (2–4 per cent. in tea, from which it may be separated by careful sublimation); **piperine**, in pepper; **nicotine**, in tobacco (up to 7 per cent. in Virginia tobacco; 2–3 per cent. in Maryland and Havana tobacco); **cocaine**, in the leaves of the Peruvian *coca* plant (not to be confused with the *cocoa* plant, which is entirely different); **morphine**, **narcotine**, and other alkaloids in opium (the dry juice of the Oriental poppy); **quinine** and **cinchonine** in Peruvian bark (now really grown mostly in the East Indies, especially Java); **strychnine** and **brucine** in the

seeds called *Nux vomica*; **aconitine**, a very poisonous alkaloid in aconite; **veratrine** in white hellebore; **atropine** and **hyoscyamine** in the deadly nightshade (used for dilating the pupil of the eye); **scopolamine** and **hyoscine** in the *Datura meteloides*; and others. All the alkaloids are poisonous, some in very small doses, but they are very valuable medicines.

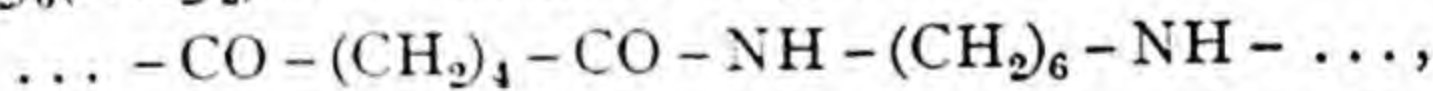
**Modern plastics.**—The older plastics from casein (p. 545), Bakelite (p. 510), nitrocellulose (p. 499), in the forms of celluloid and photographic film, and cellulose acetate (p. 500), are still much used, but many new materials have joined this group. The *polyvinyl plastics* are derived from vinyl acetate,  $\text{CH}_2 : \text{CH} \cdot \text{COOCH}_3$ , and vinyl chlorides,  $\text{CH}_2 : \text{CHCl}$ , by polymerisation, the molecules linking into chains by utilising the double bonds; thus, polyvinyl chloride is



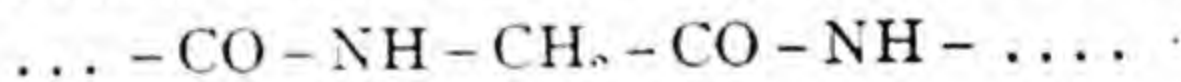
and polyvinyl acetate the same with the acetate radical  $-\text{COOCH}_3$  in place of Cl. *Polythene* is a polymer of ethylene,  $\text{CH}_2 : \text{CH}_2$ , which forms  $\dots - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \dots$ ; *alkathene* is a product of this type. From styrene (phenylethylene),  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$ , is formed by polymerisation *polystyrene*



*Perspex*, used for aeroplane windows and for lenses, is a polymer of acrylic acid,  $\text{CH}_2 : \text{CH} \cdot \text{COOH}$ . The famous *nylon* is a poly-amide formed from adipic acid (a higher member of the oxalic acid group),  $(\text{CH}_2)_4(\text{COOH})_2$ , and hexamethylene diamine  $(\text{CH}_2)_6(\text{NH}_2)_2$ , which condense to give



which is seen to have a relation to the protein structure (p. 544),





## CHAPTER XXIX

### FOODS. NUTRITION. BIOCHEMISTRY

**Foods and diet.**—We know that a green plant grows entirely from inorganic materials (p. 420). It *synthesises* carbohydrates, fats, and other organic compounds from carbon dioxide in the air, water, and mineral salts in the soil. The problem of animal nutrition is much more complex: animals cannot synthesise the organic constituents of their tissues from inorganic components, although they have limited synthetic powers: they can synthesise fats from carbohydrates. An animal requires food, which may be defined broadly as material consumed for the purpose of: (i) supplying energy and heat, and (ii) building up and repairing the tissues of the body. The requirements of nutrition are five: the food must supply:

(1) ENERGY-PRODUCING BODIES, serving as fuel and producing energy—there are two groups of these:

- (a) **Carbohydrates** (starch; sugars), which serve as fuel and are partly *transformed* into fat; and
- (b) **Fats** (animal and vegetable, such as butter and olive oil) which serve as fuel and are partly *stored* as fat in the tissues.

(2) **PROTEINS**, which may be regarded as the main constituents of lean meat, eggs, fish, gluten of flour, and some parts of vegetables. Since they all contain nitrogen (and sulphur), and since albumin (white of egg) is a typical protein, these bodies are sometimes called **albuminous** or **nitrogenous** foods. Proteins build and repair tissues, but may also serve as fuel when a little fat or carbohydrate is present, and is oxidised along with them in the body.

(3) **MINERAL SALTS**: common salt, potassium and calcium phosphates, traces of iodine (*q.v.*), etc. These go to the formation of bones, take part in digestion, and are very closely connected with the numerous processes of the body (*e.g.*, the blood

must contain certain amounts of salts, the thyroid gland must secrete thyroxine, etc.).

(4) WATER: a great proportion of the body is water.

(5) OXYGEN is not usually regarded as a 'food,' yet it is essential for the production of heat. Some lower organisms (certain bacteria) can live in absence of free oxygen and are called *anaërobic*.

(6) VITAMINS: *accessory food substances*, without which in small quantities the body cannot live even if provided with carbohydrates, proteins, salts, water, and oxygen. Just as a motor-car will soon stop and have its mechanism ruined if not provided with lubricating oil, although this does not supply the driving energy, so the animal body sickens and dies without vitamins. It is only recently that their great importance in nutrition has been recognised.

From one point of view we may compare the body with an *engine*, the fuel of which supplies its energy. Yet the animal is a self-building, self-regulating and self-repairing machine, and is the laboratory in which the most surprising and wonderful chemical changes are constantly taking place. The study of these is often called **Biochemistry**: it includes particularly the knowledge which Physical Chemistry and Organic Chemistry have contributed to the elucidation of the chemical changes in the body, many of which were formerly regarded as the results of the action of a mysterious 'vital force.' Since many of the organic compounds which were at one time thought to be formed exclusively by the action of the 'vital force' have been synthesised in the laboratory, and since many of the processes which seemed to be inexplicable, except as manifestations of 'life,' are now known to depend on physico-chemical equilibria, it has become customary to attempt to proceed as far as possible in the explanation of life-processes without assuming actions not familiar in the metamorphoses of unorganised Nature. A limit, however, is soon reached, and we cross the boundaries of Physiology and Psychology. No organic compound ever synthesised or extracted from a living plant or animal has ever shown the faintest sign of 'life,' and no system of materials ever arranged has proved capable of growth.

**Diet.**—The different kinds of food taken together constitute diet, and a satisfactory diet must: (i) have sufficient energy value—'adequate calories'; (ii) contain minimum amounts of adequate proteins, carbohydrates, fats, salts, and vitamins; (iii) conform to the dietetic habits of the nation.



A standard of food consumption with a mixed diet for an adult has been given as : protein 4 oz., fat 3 oz., carbohydrate 15 oz., per day, reckoned in *dry* weight. Water, salts, and oxygen (from respiration) are assumed to be supplied as well. Such a 'typical diet' consists of about one-sixth of protein, one-sixth of fat, and two-thirds of carbohydrate. It should be emphasised that (as is more fully explained on p. 546) the requirements of adults and children are different. The relative protein requirements of growing children are larger than those of adults, since an adult, even if performing hard manual labour, can get energy from carbohydrates and fats, but these will not enable a child to grow. It is unfortunate that, as a result of lack of knowledge about foods, the protein is consumed by adult manual workers, and young children do not get an adequate supply of meat, eggs, and fish, and fish may be white and boiled instead of fried, bacon fat (deficient in vitamin A) may be given instead of butter, and jam is given on bread instead of butter. Sweet and starchy food is provided in excess of requirements, and the child may grow fat, yet is liable to lung and eye infections. A great deal of detailed and accurate information is now available as a result of experience in war-time rationing, and it is likely that a more scientific outlook on diet may result from better education in such matters in schools.

We must now consider briefly the various parts of diet, and since carbohydrates form the largest part we may begin with them, although the proteins were formerly regarded as pre-eminent—hence the name, which is derived from a Greek word meaning 'to take the first place.' Recent researches have deposed the proteins from the exaggerated importance attached to them by Liebig and still upheld by many persons who have not followed the progress of science.

**The carbohydrates.**—These substances, the first products of plant synthesis, usually form the most abundant and economical source of energy. The Eskimo, who has no cereal foods, is compelled to consume the enormous quantity of 15 lb. of meat in less than 14 hours in order to obtain his heat and energy! The various carbohydrates and other sugars are first converted into glucose by hydrolysis by enzymes. The sugar, which ultimately finds its way into the blood, is constantly undergoing oxidation and replacement, and over half the energy supply of the human body is normally derived from the oxidation of



glucose, ultimately to carbon dioxide and water. In the disease of diabetes the glucose of the blood is not oxidised.

The process by which glucose is oxidised is a complicated one, and a number of stages are passed through before carbon dioxide and water are reached. The glucose molecule is first broken up into simpler parts and these then undergo oxidation. It is thought that the glucose must first be combined with phosphoric acid, and it is not impossible that alcohol is an intermediate step in the oxidation process. The oxidation occurs in the muscles and the agency of a substance called **insulin**, which is secreted into the blood by the islet cells of the pancreas, is essential: insulin is therefore used in the treatment of diabetes.

**Cane sugar** is not hydrolysed either by the saliva or the gastric juice and passes to the intestine, where it is hydrolysed by the same enzyme, *sucrase*, as is present in yeast (*q.v.*), but which is now supplied by a juice secreted by the intestine, into glucose and fructose, which are absorbed into the blood. **Starch** is more easily hydrolysed and hence more easily digested, especially when cooked, *i.e.*, brought into the form of a colloidal solution, although raw starch can be digested. The starch is hydrolysed into dextrin and maltose by an enzyme called **ptyalin** (probably the same as diastase, p. 503) in the saliva, which is only active in weakly alkaline solution. The action of the saliva goes on for some time after the solid food is swallowed, since segregation prevents for some time the acid gastric juice in the stomach from putting the ptyalin out of action. A further hydrolysis of starch occurs in the intestine, by means of a starch-splitting enzyme in the pancreatic juice, called **pancreatic amylase** or **amyllopsin**, perhaps merely a variety of diastase (amylase, p. 503).

**Cellulose** is not digested in the human body, but it gives bulk ('roughage') to food and assists its passage along the digestive track. Herbivora, *e.g.*, horses, can digest cellulose in the form of hay and straw, as a result of bacterial action in the intestines.

**Fats.**—Fats, sometimes called **lipides**, constitute a more concentrated form of energy fuel than carbohydrates, and excess of food beyond the energy requirements may be stored in the tissues in the form of fat to provide a fuel reserve—the spare petrol tin of the human motor. Fats are formed in plants probably, and in animals certainly, from carbohydrates, and fat taken as such in food is also deposited in the tissues. During starvation the sugar in the body is quickly used up, and the fat reserve is then called upon. Some fats in the body contain



derivatives of phosphoric acid and are called **lecithins**: others contain nitrogen or sulphur compounds. These complex fats occur in milk and in the more highly organised cells of animals or plants, egg-yolk, brain, nerve-tissue, seeds, etc. Proteins, taken in excess, may also contribute to the formation of fat in the body.

**Proteins.**—The principal constituents of muscle or lean flesh are proteins, which are very complicated compounds containing carbon, hydrogen, oxygen, nitrogen, and sometimes phosphorus, and sulphur, with molecular weights greater than 10,000, and are mostly colloids. They are essential constituents of both plant and animal cells and there can be no life without proteins.

Plimmer has compared each kind of protein, which has a very complicated chemical structure and is built up of about twenty simpler 'units,' with a string of beads of twenty colours. On digestion the string is broken and the separate beads pass into the circulating blood.

Each tissue or organ has a special protein pattern and collects only the kinds of beads which it wants to assemble this pattern. Animal proteins contain the beads in the most suitable proportions. Beads which do not fit into the patterns, or any excess beads, are burnt up as fuel. Plant proteins contain the same kinds of beads as animal proteins but in quite different proportions. Some kinds are present in excess and others may be scarce or absent.

Plants synthesise their proteins, but animals must get their proteins ready formed, either from plants or animals.

During the War, when the shortage of protein foods became acute in Germany, the rapid growth of micro-organisms, in which proteins are built up, was utilised. 'Mineral yeast,' a species of *Torula*, grows rapidly on a liquid containing sugars and ammonium salts, building up proteins, and the organism *Endomyces vernalis* can build up a product containing fat, proteins and carbohydrates.

More than fifty kinds of protein have been isolated and studied and there are probably enormous numbers of them. As far as we know, every kind of protein can be broken up by hydrolysis (p. 493) into a number of simpler molecules, just as starch may be broken up into numbers of glucose molecules, but the simpler molecules from the protein are not all alike, as are the glucose molecules. The simpler molecular components of the large protein molecule are called **amino-acids**, because each molecule contains the **amino-group**  $-NH_2$ , and the **carboxyl radical** of all



organic acids,  $-\text{COOH}$ . Thus they act at the same time as weak bases (because of the presence of the residue of ammonia,  $-\text{NH}_2$ ) and also as weak acids, because of the  $-\text{COOH}$  group. The proteins seem to contain substituted polypeptide chains of the type  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}-$ .

About twenty different kinds of amino-acids have been distinguished in various kinds of proteins, different proteins containing different groups of amino-acids. It has been calculated by Abderhalden that these twenty amino-acids could form at least 2,432,902,008,176,640,000 different compounds, so that there is every possibility of building up the great number of proteins found in plants and animals, each showing specific reactions in respect of antibody formation (p. 556), from a few simpler constituents.

Not all animal proteins can serve in nutrition: egg albumin, for instance, contained in white of egg, can serve as a sole protein food, but gelatin cannot. The body can make its amino-acids from other proteins, with one or two exceptions. These exceptional amino-acid groups must be supplied to it ready made, and they are not in gelatin.

Although proteins can supply heat, as mentioned, this is not economical, since heat may be more cheaply, and probably more easily, developed by carbohydrates and fats. Manual workers do not require large amounts of meat, but can just as well obtain their energy from fats and carbohydrates.

A familiar protein is **albumin**, contained in solution in the white of egg. It is a colloid but has been obtained in a crystalline form. Sørensen has determined the molecular weight of albumin as 34,000 by direct osmotic pressure measurement, and the same value has been found by Svedberg by a sedimentation method. Albumin is coagulated and rendered insoluble in water by heating. Vegetable albumins are synthesised in plants from inorganic materials.

An industrially important protein is **casein**, obtained from *milk*. It is separated from milk, from which as much cream as possible has been removed, by adding an acid such as sulphuric or acetic, or by *rennet*, an extract from the mucous membrane of the stomach of the calf containing an enzyme **rennin**, which is somewhat similar to pepsin (p. 551). The curd is separated, washed, and dried. Casein is a protein containing about 0.8 per cent. of phosphorus; it is insoluble in water and is supposed to be contained in solution in the milk in the form of a soluble calcium salt, since it is acidic in character and dissolves in weak alkalis.



Casein is used in making patent foods (*Plasmon*, *Sanatogen*, etc.) and casein plastics. The latter are produced by mixing coagulated casein with formaldehyde and subjecting the mass to great pressure, when it forms a hard solid called *galalith*, similar to horn, from which combs, imitation amber and ivory, electrical insulators, umbrella handles, buttons, etc., are made. Unlike celluloid it is not inflammable, but it is not elastic. Casein is also used in making size and (mixed with slaked lime and pigments) water paints. It is a constituent of *cheese*, which is made by curdling a partly soured milk (except for soft cheeses, when fresh milk or cream is used) with rennet, pressing the curd (which contains the butter fat) and allowing it to 'ripen,' when various enzymes act upon it, rendering it digestible and palatable. Camembert and Limburger cheeses contain small amounts of indole, a substance of unpleasant odour. Gorgonzola and Stilton cheeses contain growths of a mould, *Penicillium glaucum*.

**Energy values of foods.**—The energy value of a food may be determined by burning it with oxygen in a calorimeter. Experiments made by Atwater and others have proved (as we should expect) that the heat evolved in the calorimeter is the same as that given out by foods during combustion in the body. This was suspected by Lavoisier, who carried out experiments on respiration (Fig. 283), which were interrupted by his untimely death.

The average heats of combustion in kilogram calories per *gram* are: carbohydrates 4; fats 9; proteins 4, when full allowance for incomplete oxidation (*e.g.*, proteins only to the stage of urea,  $\text{CON}_2\text{H}_4$ ) and incomplete digestion, is made. Thus a gram of fat (*e.g.*, butter or margarine) will furnish as much energy as over two grams of protein or carbohydrate. The corresponding numbers in kilogram calories per *pound* (rounded off) are: fats 4000, carbohydrates 1800, proteins 1800.

Muscular energy can just as well be got from fats and carbohydrates as from proteins, and 'any reasonable combination of foodstuffs given in sufficient abundance to meet the energy requirements will almost certainly supply an ample amount of protein' (Sherman). Since fats and carbohydrates can replace protein except for nitrogen maintenance, there is a **minimum protein requirement**, which has been estimated 'on a generous basis' as 1.6 oz. per 154 lb. (11 stones) body weight per 24 hours.\* The energy requirement for a man absolutely at rest

\* Sherman. Other figures are 2.1–5.3 oz., with an average of 3.6 oz., and there is still some difference of opinion on the matter.

has been estimated as 2000 kg. cal. per 24 hours ; this is called the **basal metabolism**. The extra energy required as food depends on the amount of work done. About 10 per cent. must be added to the food as purchased to allow for waste and refuse. The following figures are the *net* energy and *food* (the first figure increased by 10 per cent.) requirements for different classes of workers, in each case for an 'average man' of 25-50 years of age, weight 145½ lb., height 5 ft. 7·4 in., in good health.

<i>Type of worker</i>	<i>Energy requirement in kg. cal.</i>	<i>Food requirement in kg. cal.</i>
Tailor - - - -	2500	2750
Bookbinder - - -	2800	3100
Metal worker or carpenter	3200	3500
Painter - - - -	3250	3600
Stonemason - - -	4400	4850
Woodcutter - - -	5000	5500

The average male brain worker is amply supplied by a diet yielding 2200-2600 kg. cal. ; the average working woman requires 2650 kg. cal. per day, and the sedentary woman 2100 kg. cal. Growing children require large amounts in proportion to their weight : a boy of 16-20 years of age requires 3800 kg. cal., and 3200 kg. cal. at the age of 13-15, as much as an adult manual worker. A girl of the age 16-20 requires 2400 kg. cal., with 2800 at the age of 13-15. Nursing mothers also require more food than that quoted for average women.

The weights of various foods necessary to supply the energy requirements are given below in oz. to supply *one hundred* kg. cal. :

Beefsteak	- 2·3	'Whole' wheat	1·0	Apples	- - 5·6
Lean ham	- 1·2	Wheat flour	- 1·0	Almonds	- 0·5
Bacon	- - 0·6	White bread	- 1·3	Olive oil	- 0·4
Salmon	- - 1·7	Cabbage	- 11·1	Sugar	- - 0·9
Oatmeal	- - 0·9	Potatoes	- 4·2		

The chart in Fig. 340 gives the compositions of some common foods.

**Mineral requirements.**—The percentage composition of the average human body is as follows :

O	C	H	N	Ca	P	K	S	Na	Cl	Rest
65	18	10	3	1·5	1	0·35	0·25	0·15	0·15	1·6

To supply the mineral requirements the day's food will probably contain 0·8-1·87 gm. of calcium, 0·14-0·67 gm. of magnesium,



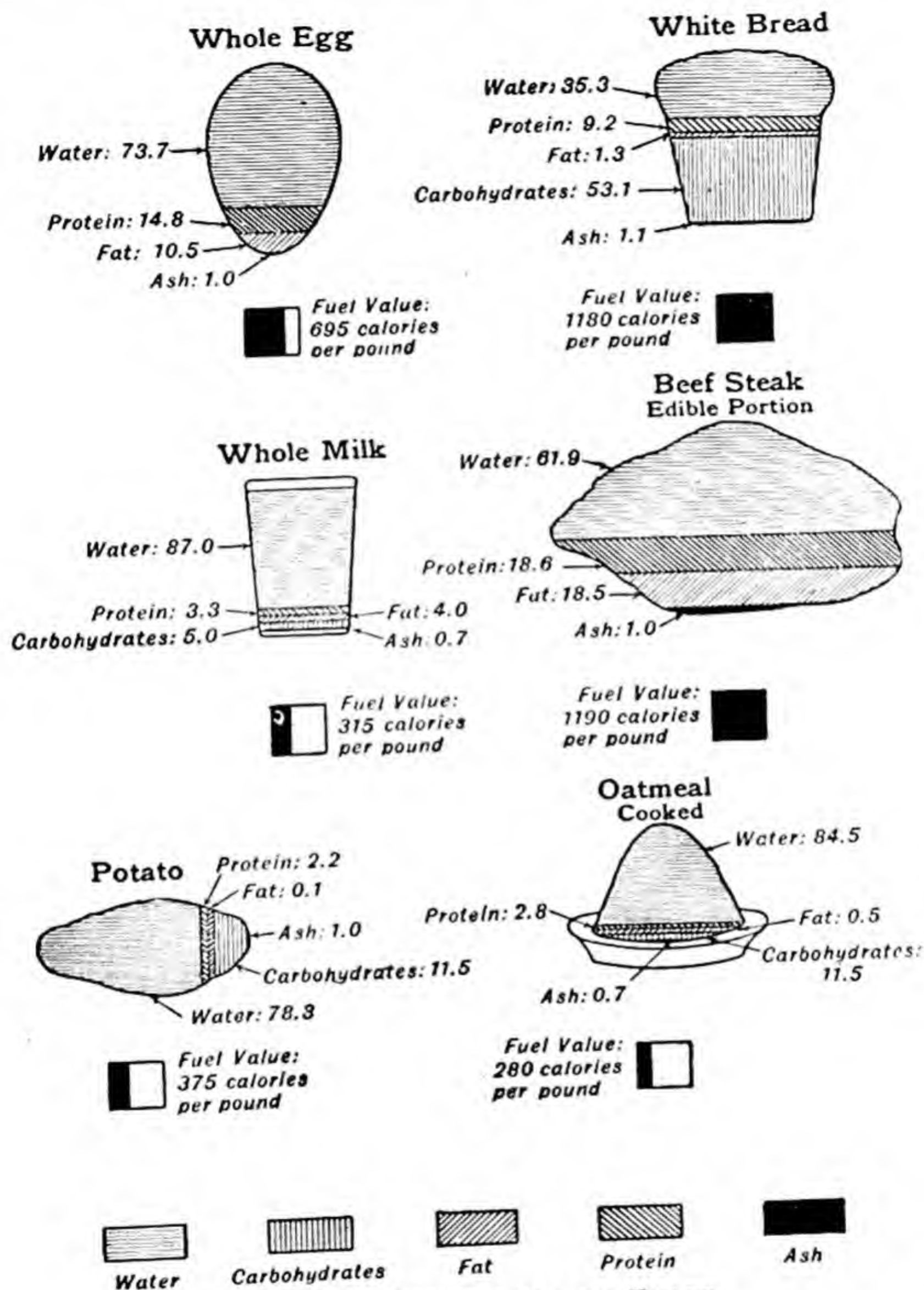


FIG. 340.—COMPOSITION OF FOODS.

0.015 gm. of iron, and 1.43–6.54 gm. of potassium. The calcium requirement (for bone) may not be met, especially in growing children, if unsuitable foods are taken. The body can probably supply all its phosphorus requirements from inorganic phosphates in food.

Another important mineral requirement is *iodine*. *Iron* is also essential for the red haemoglobin of the blood and cell nuclei.

Wholemeal contains more iron than white bread, yet less iron is absorbed from a wholemeal than from a white bread diet, this being the result of a larger amount in the former of phytic acid, which also hinders calcium absorption, and calcium carbonate has been added to wholemeal flour. In addition to its dietetic value, a high protein intake improves the absorption of iron, and meat and fish are also the main sources of nicotinic acid, one of the B vitamins (p. 550). Low protein diet decreases resistance to disease and may be associated with mental confusion and diarrhoea.

**Vitamins.**—Since about 1912 it has become clear that the health and growth of animals are dependent upon the presence in food of *small* amounts of substances to which the name vitamins has been given. These are present in *fresh* foods of various kinds. The fact that fresh foods or fruit juices are necessary for the preservation of health has long been known in the case of men making long sea voyages in which preserved foods, such as salt pork, or wheat flour, are often the only ones available.

Lind, an English writer on scurvy, knew in 1757 that it was prevented by lemon or orange juice (lime juice is much less effective). Captain Cook in 1772 kept his crew in good health in a voyage of three years by giving them fresh food (scurvy is also prevented by freshly killed meat), whilst Vasco da Gama in his voyage round the Cape of Good Hope in 1498 lost 100 men out of 160 from scurvy. This disease was eliminated in the Navy in 1795 by a daily issue of 1 oz. of lemon juice,  $\frac{3}{4}$  oz. being found insufficient. Cod liver oil was used to cure rickets in Manchester Infirmary from 1772.

In Asiatic countries where rice is largely eaten, a disease called beri-beri (a form of polyneuritis) may develop by the use of white or polished rice, the vitamins being present in the rice germ or embryo, which is removed in polishing. Birds fed on polished rice develop polyneuritis, but are rapidly cured by feeding with whole rice or rice polishings.

Several vitamins are now known in the pure state and many have been synthesised.

**Vitamin A** (formerly called *fat-soluble A*) promotes growth ;



without it or with a deficiency of it, animals do not grow. It accompanies many, but not all, fats and oils, such as cod liver oil, butter, and the fat in egg yolk, but is not found in lard, pork and bacon fats, olive oil and margarine made from vegetable fats only. It occurs in green leaves such as spinach and clover. The cow obtains the vitamin A of butter fat from green vegetable food, and the source of vitamin A in fish is also ultimately vegetable, viz., the phytoplankton in the sea. The only part of the fish rich in vitamin A is the liver, and halibut liver oil is considerably richer in it than ordinary cod liver oil. The next richer sources are fish roe, butter and egg yolk; smaller amounts are present in milk, carrots, green vegetables and tomatoes. The dietary factor which prevents rickets is not vitamin A, but vitamin D. Deficiency in vitamin A in the diet is associated with a lowered resistance to bacterial infection. The existence of vitamin A was established independently in 1913 by McCollum and Davis and by Osborne and Mendel.

Vitamin A is fairly resistant to heat and is present, in diminished amounts, in cooked foods which contain it in the raw state. The amount of vitamin A in a fat or oil is estimated from the intensity of the blue colour produced by antimony trichloride. Vitamin A can be separated by distillation of the unsaponifiable part of the oil under very low pressure (0.0001 mm.). The formula of pure vitamin A is  $C_{20}H_{30}O$ .

The pigment *carotene*, found in carrots, has been separated into three violet-coloured isomers, with the formula  $C_{40}H_{56}$ , called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carotenes, the  $\beta$ -carotene predominating in nature: it is converted in the body into two molecules of vitamin A, whilst  $\alpha$ - and  $\gamma$ -carotenes give rise to one molecule only.

*Visual purple*, a pigment related to carotene, is contained in the retina of the eye, and deficiency of vitamin A is associated with a retardation in regeneration of visual purple, and night blindness.

**Vitamin B** (formerly called *water soluble B*) is also important in promoting growth. It is widely distributed in many natural foods, especially in plants, and occurs in yeast, in the germ of rice and of wheat, in nuts, fruits, spinach, and plant roots, but not in polished rice or white flour, although it is present in whole wheat flour. The effects of vitamin B were recognised by Eijkman in Java in 1897. Goldberg and Lillie in 1926 and others since have shown that vitamin B consists of several factors.

**Vitamin B<sub>1</sub>** promotes growth and prevents beri-beri; it is deactivated by heating at 120-130°. Synthetic crystalline vitamin B<sub>1</sub> is  $C_{12}H_{17}ON_4SCl, HCl, \frac{1}{2}H_2O$ , derived from the free base



$C_{12}H_{17}ON_4S(OH)$ . **Vitamin B<sub>2</sub>**, deficiency of which leads to blurred vision, dermatitis, loss of hair, pellagra, and general lowered tone of health, is strongly fluorescent and is identical with the yellow pigment **riboflavin** or *lactoflavin*,  $C_{17}H_{20}O_6N_4$ , present in milk whey (1 gm. in 10 tons); it is stable at  $120^\circ$ . **Nicotinic acid** is  $C_6H_5O_2N$ , deficiency of which leads to pellagra, and in severe cases hallucinations and dementia. **Vitamin B<sub>6</sub>**, or *pyredoxene*, is  $C_8H_{11}O_3N$ , which relieves certain neuro-muscular symptoms and some types of muscular dystrophy.

**Vitamin C** (*water soluble C*) is the *antiscorbutic vitamin*, preventing scurvy. The principal sources are fresh fruits and vegetables, especially paprika (Hungarian red pepper), lemon, orange and tomato fruits; the juice of tinned tomatoes, cooked in the absence of air, is still quite rich in vitamin C, although it tends to be destroyed on cooking or storing food. It is also present in fresh-killed meat and fresh milk, but pasteurised milk may lead to scurvy in children unless accompanied by orange juice. The potato is a poor source of vitamin C, but one orange a day provides an adequate supply of it. The acid in lemon juice does not prevent scurvy, as it may be neutralised and precipitated by adding chalk without affecting the vitamin C content of the juice. Vitamin C is widely distributed in plants and animals; it is more stable in acid solution. It is identical with the crystalline *ascorbic acid*,  $C_6H_8O_6$ , isolated in 1920 by Szent-Györgi from thymus and adrenal glands and later from fresh paprika fruit.

**Vitamin D** (*antirachitic vitamin*), discovered by Mellanby in 1921, prevents rickets and is a powerful growth stimulant. Rickets is due to lack of calcium phosphate deposition in bones. Vitamin D is present in fish liver oils, yeast, fat and butter. Its action is dependent upon an adequate supply of vitamin A.

Steenbock and collaborators showed in 1924 that fats and oils became antirachitic on exposure to ultra-violet light, and that this was associated with the presence of a precursor called a sterol. One such precursor is *ergosterol*, which is present in ergot of rye, yeast and fungi, another is a derivative of *cholesterol* (a constituent of brain tissue), and each yields a corresponding form of vitamin D on exposure to ultra-violet light. Irradiated sterol preparations for human use are on the market. The crystalline *calciferol*,  $C_{28}H_{44}O$ , isolated from irradiated ergosterol, is known as vitamin D<sub>2</sub>; it is toxic in large doses and its activity is destroyed on heating at  $190^\circ$  or by prolonged irradiation. Vitamin D is normally formed in the body by exposure of the skin, which contains sterols, to direct sunlight.



Vitamin E, discovered by Evans and Bishop in 1922, is the fertility vitamin. It is present in many kinds of animal tissue, milk, leaves of plants, the wheat germ, etc. The oil of the wheat embryo is especially rich in vitamin E, and has yielded three active substances,  $\alpha$ -,  $\beta$ - and  $\gamma$ -*tocopherols*, which are closely related oxygen-ring compounds showing vitamin E activity, the  $\alpha$ -form being most active.

**Hormones.**—The internal glands in the body produce secretions which sometimes contain physiologically important substances called hormones. **Thyroxin**,  $C_{15}H_{11}O_4NI_4$ , which has been synthesised, is secreted by the thyroid gland (p. 334), and deficiency of it gives rise to cretinism and myxoedema, both of which can be cured by giving thyroid preparations. The thyroid gland may contain other physiologically active iodine compounds. Lack of iodine in the diet causes enlargement of the thyroid gland, producing goitre. **Adrenalin**,  $C_9H_{13}O_3N$ , is secreted by two small glands known as the adrenals, or suprarenal bodies, lying above the kidneys. Adrenalin increases the pressure of the blood and stimulates the sympathetic nervous system. It is used in conjunction with local anaesthetics (p. 9). It exists in two optically active forms (p. 514), the natural compound being laevo-adrenalin, which is twelve times as active physiologically as dextro-adrenalin. **Insulin**, which is probably a complex protein derivative and (unlike thyroxin and adrenalin) has not been synthesised, is produced in the pancreas (p. 542). Deficiency of insulin gives rise to diabetes, which is treated by hypodermic injections of insulin.

**Digestion.**—With the provision of suitable food the problem of nutrition is solved by the agency of a number of processes in the body which constitute digestion. There were two early theories of digestion. Van Helmont (1644) assumed that it was closely related to fermentation, whilst Pitcairn (1652-1713) considered that it was a process of mechanical trituration, the force of the muscular walls of the stomach being estimated at 12,951 lb. Réaumur showed that food enclosed in perforated silver spheres could be digested in the stomach, and Spallanzani found that the gastric juice outside the stomach could digest food, so that the mechanical theory was shown to be incorrect. In 1836 Schwann showed that the solvent power of the gastric juice was due to a particular substance, **pepsin**, an *enzyme*.

The process of digestion begins in the mouth, where an enzyme in the saliva, **ptyalin**, begins to hydrolyse starch into maltose. This process, which goes on in the weakly alkaline saliva,

continues for  $\frac{1}{2}$ -2 hours in the stomach, since owing to segregation the swallowed food does not mix immediately with the acid gastric juice, which would arrest the activity of the ptyalin. By the motion of the walls of the stomach the food is gradually pushed towards the pylorus, or entry to the intestines. In its passage it becomes mixed with the gastric juice, containing 0.4 to 0.5 per cent. of free hydrochloric acid, and the enzyme pepsin

present in the juice secreted by the walls of the stomach. The pepsin hydrolyses the proteins to some extent, splitting them into soluble simpler fragments called **proteoses** and **peptones**. The acid semi-fluid mass of partly digested food, called *chyme*, is passed in portions through the pylorus into the small intestine. Usually all the food has passed through the stomach in 6 or 7 hours.

The chyme lies in the curve of the duodenum of the small intestine, where it becomes mixed with three fluids: (i) bile from the gall bladder, (ii) pancreatic juice from the pancreas, and (iii) intestinal juice from the walls of the small intestine. These are all alkaline and neutralise the acidity of the gastric juice. The outflow of pancreatic juice occurs as soon as the acid

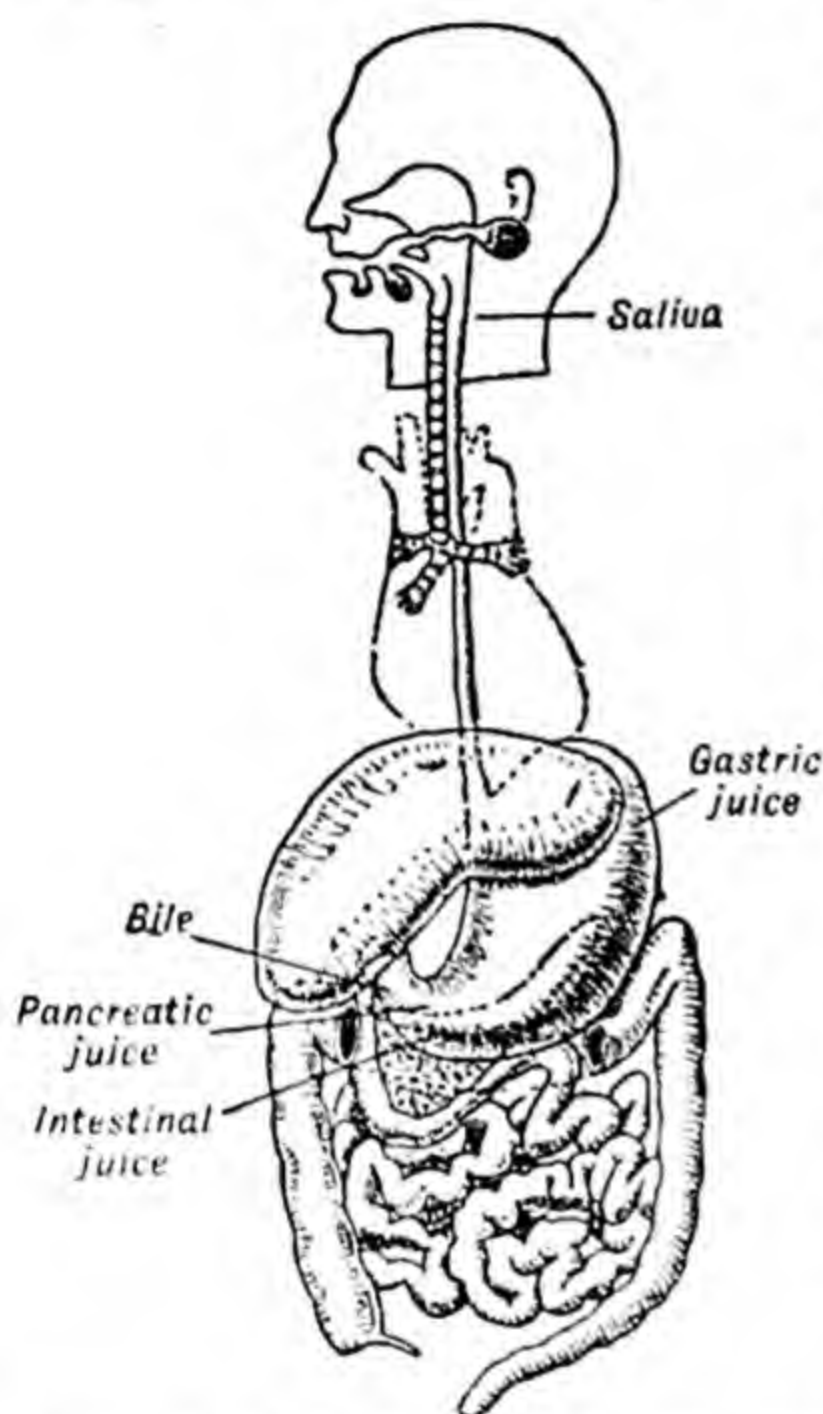


FIG. 341.—DIAGRAM OF DIGESTIVE SYSTEM.

chyme, entering through the pylorus, acts on some constituent of the mucous membrane of the intestine and produces a hormone called **secretin**, which is absorbed by the blood, passes in the blood stream to the pancreas, and stimulates the flow of pancreatic juice. The hormone is thus a material messenger carried in the blood to the pancreas to announce that the assistance of the latter is required. The pancreatic juice contains in alkaline solution three enzymes: **trypsin**, **amylase**, and **lipase**. The bile, slightly alkaline, is secreted by the liver and is poured out from the gall bladder into the intestine.



It probably acts by emulsifying fats so as to bring them into intimate contact with enzymes. The intestinal juice is distinctly alkaline and contains the enzymes **erepsin**, **sucrase**, **maltase** and **lactase**, and the co-enzyme **enterokinase**.

The amylase of the pancreatic juice splits starch into maltose (malt sugar); the trypsin splits proteins into proteoses, peptones, and amino-acids; and the lipase splits fats into fatty acids and glycerol. The erepsin of the intestinal juice splits peptones to amino-acids and perhaps even ammonia; the sucrase splits cane sugar into glucose and fructose; the maltase converts maltose to glucose; the lactase converts lactose (milk sugar) to glucose and another sugar called galactose; and finally the enterokinase acts on the trypsin in the pancreatic juice, which is present in an inactive form called **trypsinogen**, and converts it into active trypsin. This is an example of one enzyme activating another. The secretion of the intestinal juice, like that of the pancreatic juice, is stimulated by hormones.

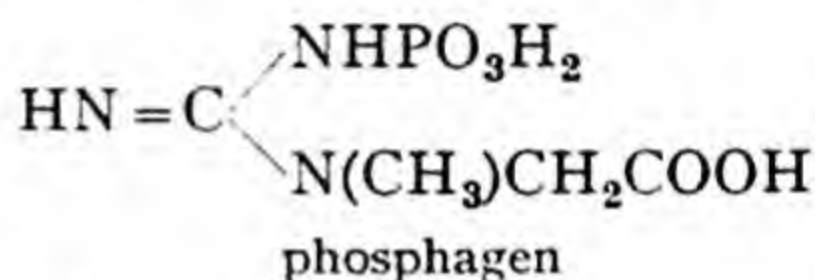
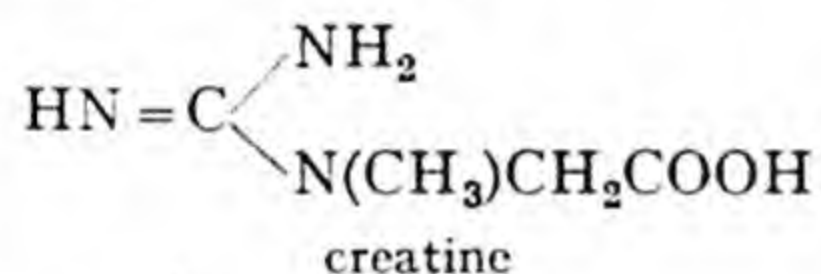
As a result of the action of the ten enzymes named (and possibly others), the carbohydrates of the food have been converted into glucose, the fats into fatty acids and glycerol, and the proteins into amino-acids. Absorption of these into the blood then occurs through the walls of the intestine, whilst the residue of the food passes the ileocaecal valve into the large intestine. The walls of the latter secrete an alkaline liquid which helps the completion of the digestive changes, but so far as is known, no other enzymes are secreted by the large intestine. Water is absorbed and the material solidifies to faeces which are excreted. In the large intestine the food residue is subjected to the influence of vast numbers of bacteria. These do not assist digestion but do not do any harm—they perhaps check the development of other, harmful, organisms.

We must now consider what happens to the glucose, fatty acids, glycerol, and amino-acids into which the food has been resolved. Much of the glucose, taken into the blood from the capillaries of the intestinal wall and to the portal vein, is stored in the liver in the form of a peculiar starch-like substance called **glycogen**, which was discovered by Claude Bernard in 1857. It has the empirical formula  $(C_6H_{10}O_5)_x$ , is a white amorphous powder like starch, but forms a colloidal solution with *cold* water. It is hydrolysed by dilute acids to yield glucose. The reserve store of glycogen gradually passes into the blood again as glucose produced from glycogen by an enzyme in the liver. Glucose is oxidised in the muscles so as to produce *ultimately*

carbon dioxide and water (p. 424) and heat. Some of it may also produce fat, which is stored in the tissues. Glycogen is also stored in muscles.

The mechanism of the contraction of muscle and the source of muscular energy are not at present very clear and are probably complex in detail. It was formerly thought that *lactic acid*,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , and phosphoric acid were formed during the contraction of muscle, the lactic acid passing back into glycogen during the relaxation period, and at the same time some glucose formed from the glycogen with the lactic acid was supposed to be oxidised. An outline of the modern explanation is as follows.

The muscles of vertebrates contain about 0.4 per cent. of *creatine*, an aminoacid (p. 543) isolated from meat extract by Chevreul in 1843. This forms with phosphoric acid the com-



pound creatine phosphoric acid, or *phosphagen*. The energy of muscle contraction is derived from the splitting of phosphagen, which is re-synthesised during the muscle recovery phase. The energy for this synthesis is 120 cal. per gm.  $\text{H}_3\text{PO}_4$ , and is derived from the breakdown of glycogen into lactic acid, 200 cal. per gm. lactic acid. In presence of oxygen the lactic acid disappears, mostly by re-synthesis of glycogen, although some is oxidised.

We must next consider what happens to the fatty acids and glycerol formed by the digestion of fats. These recombine *after* passage through the walls of the intestine to form fats, which, in very fine globules, are taken up by the lymph vessels and poured into the blood with the lymph. It seems as if it were necessary for the fats to be split into fatty acids and glycerol in order to get them to pass through the intestinal wall. The re-formed fat then passes to the tissues from the blood. The fatty acids may be redistributed in the recombination process.

The amino-acids are regrouped to form body tissues in the way described. Those not required are decomposed by enzymes in the liver; the nitrogen is split off in the form of ammonia,



and this, with the carbonic acid always present in blood, is converted into urea,  $\text{CON}_2\text{H}_4$ , which is excreted in the urine. In this way the waste proteins are got rid of.

It will be seen that the series of chemical changes occurring in the animal body during the digestion of food is very complex and extremely interesting. It is obviously impossible to consider any further details here. Only a minor part of the digestive process occurs in the stomach, which, as has been shown by direct observation, is not essential to digestion and secretion.

**Pathological chemistry.**—The chemical changes occurring in the body in a state of health have been briefly considered. In disease, other conditions arise which, in so far as they may be explained by chemical changes, form the subject of **pathological chemistry**. For many centuries the guiding theory in medicine was the **humoral pathology** associated with the name of Hippokrates (450 B.C.), in which it was assumed that disease was caused by disturbances in the proportions and properties of **four humours**: blood, bile, phlegm, and black bile (the latter still living in the word melancholy). This theory was especially developed by Galen (131-201 A.D.; p. 62) and by the Arabic physicians. It was for long the principal guide in European medicine, which was at first largely derived from Greek sources as systematised by the Arabs.

Van Helmont (1577-1644) says that he studied the works of Galen and Hippokrates, 'noted all that seemed certain and incontrovertible, but was dismayed, upon revising my notes, to find that the pains I had bestowed and the years I had spent, were altogether fruitless.' He adopted some of Paracelsus' views, and in particular was of the opinion that ferments played an important part in the processes of the body, an idea which contained a large element of truth. He considered that the acid of the gastric juice was necessary for digestion, but an excess of acid caused discomfort and illness, since it could not be neutralised by the alkali in the duodenum. He compared the interactions of the various juices of the organs with similar reactions of solutions outside the body.

The discovery of micro-organisms by Leeuwenhoek in 1683 was not sufficiently attended to, but by the beginning of the nineteenth century it was becoming clear that diseases are frequently caused by the poisonous substances (**toxins**) produced by micro-organisms, bacteria, which have entered the body by infection, and are often specific in particular diseases. The



work of Pasteur and Koch was especially important in the development of this study.

**Immunity.**—Since the living body is constantly exposed to bacteria, it is clear that there must be some function of the living tissue which enables it to resist the attacks of its bacterial invaders. This is called **immunity**. It is now generally admitted that immunity is mostly secured by the manufacture of chemical substances of unknown composition in the tissues, and that these act on the living bacteria. When the blood serum (*i.e.*, the clear liquid in which the blood corpuscles are suspended) of a patient recently recovered from typhoid is added to a suspension of living typhoid bacilli, the latter lose their power of movement and clump together, or become **agglutinated**: they are killed. This bactericidal action of the serum, which occurs only in presence of small amounts of salts, depends on the presence of *two* constituents in the immune serum: (i) the **amboceptor**, which unites the living bacterial cell to (ii) the agent toxic to it, called the **complement** (sometimes **alexin**). The complement is present in normal serum.

Diphtheria and tetanus bacilli produce their harmful effects by secreting and giving off soluble poisons called **toxins**. By injecting successive small quantities of suspensions of the dead bacilli into the blood of an animal, an **antitoxin** is built up, and the serum of the blood containing the antitoxin can then be used by injection as a remedy for diphtheria or tetanus. Most other bacteria, however, liberate their poisonous products only when they die and disintegrate, and they do not give them off into the blood: against these **endotoxins** no specific antitoxins have been produced. Toxins and antitoxins are specific, and although adsorption probably first brings together the toxin and the antitoxin, some chemical reaction between them perhaps occurs subsequently. Antibodies are produced by other agents than toxins, called antigens, since they give rise to antibodies, and the relation is specific. If human serum is injected into a rabbit, the serum of the latter gives a white precipitate with human serum, and to a less extent with ape's serum, but not with the sera of other animals. This can be used as a test for bloodstains.

**Antitoxin** sera act on the toxins produced by specific bacteria: the principal kinds are those used against the toxins of diphtheria, tetanus, botulism, and bacterial dysentery. **Antibacterial** sera act on bacteria themselves: the principal varieties are those of streptococcus, typhus, cholera, and tuberculosis.



Difficulty is caused in the intravenous administration of sera containing proteins foreign to human blood serum by the phenomenon of *anaphylaxis*. If a small amount of foreign protein (*e.g.*, egg albumin) is injected, the body becomes extraordinarily sensitive to a further dose of *the same* protein. A dose of 0.000,000,05 gm. of egg albumin will sensitise a guinea-pig so that it will die if 1-2 mgm. of albumin are given a week later.

The specific substance present in a serum is called the *amboceptor*: this is supposed to have the capacity of attaching itself to the bacterium or antigen on the one hand (or to the blood corpuscle in the case of serum capable of breaking down these and producing *haemolysis*), and to the complement on the other hand. When a suspension of living or dead bacteria is injected into a normal animal, it is found that the white corpuscles of the blood (*leucocytes*) collect in large numbers about the place, but the bacteria are not absorbed to any extent by the leucocytes. But if the bacteria are injected into an immunised animal, *i.e.*, one which has received injections of suspensions of the same kind of bacteria, then it is found that the leucocytes now absorb the bacteria. Leucocytes of this kind are called by Metschnikoff *phagocytes*, and the previous treatment is supposed to produce specific substances, called *opsonins*, which make the bacteria 'suitable' for ingestion by the phagocytes, when they are gradually dissolved. Blood serum contains a lipase (fat-splitting enzyme) which may be important in resisting tuberculosis, as it dissolves the fatty envelope of the tubercle bacillus.

Ehrlich supposed that the protoplasmic cells of an animal have an affinity for the substance injected (the antigen) which gives rise to the antibody, the association being caused by the joining together of two chemical groups, those on the protoplasmic molecule being called the *receptor groups*, those on the antigen the *haptophore groups*. The poisoning by a toxin is caused by the union of the haptophore groups of the toxin with the receptor groups of the protoplasm. In some cases there may not be an affinity between these: a toxin is never poisonous to *all* animals. The protoplasmic receptor groups fulfil physiological functions and when they are occupied by toxins the animal cannot fulfil these properly, but recovery ensues by regeneration of receptor groups unless the toxin dose is too large. By repeated doses of toxin, the receptor groups are formed in such large numbers that they go off into the blood and constitute the antibody. The antitoxin in the blood then

saturates the haptophore groups of the toxin so that it cannot unite with the protoplasm of the cells.

Poisons like prussic acid or alkaloids do not act as antigens, *i.e.*, they do not generate antibodies when injected into the blood, whilst toxic proteins have this property.

**Antigens** are nearly always proteins; the chemical nature of **antibodies** is unknown, but they are generally assumed to be proteins. They are formed in many parts of the body, but how, by what cells, and by what processes, is not known. Their existence is inferred from the effects they produce, as is also the case with enzymes. It is also not certain whether there are specific antibodies (agglutinin, precipitin, amboceptor), or whether a single antibody may produce the different reactions in different circumstances. It is probable, however, that there are two different groups of antibodies: (i) antitoxins, neutralising toxic antigens, and (ii) those (or, it may be, that) producing agglutination, precipitation, and lysis.

**Venoms.**—The toxic constituents of snake venom are protein in character, and are coagulated on heating like albumin of white of egg. They are complex mixtures, containing constituents which paralyse the voluntary muscles and the muscles of the heart and respiratory centres, cause solution of the red and white blood corpuscles, and destroy the anti-bacterial properties of the blood. The venom is active when injected into a blood vessel, it is rapidly absorbed by the eye, but takes some time to act if introduced below the skin, and some venoms are inactive when taken by the mouth, provided there are no cracks or abrasions. Scorpion and spider venoms are probably proteins, those of mosquitos and gnats are probably the products of bacteria and moulds in the œsophagal sacs, that of bees is a protein-free organic base. (The formic acid injected by the sting of bees, ants, etc., is probably not the active toxin.) Many fish are poisonous by their bites or by spines connected with special glands; toads and salamanders have acid and basic poisons in the skin glands, and jellyfish and sea anemones have stinging glands. Antitoxins to many of these toxins can be prepared.

**Disinfectants and antiseptics.**—The destruction of bacteria outside the body is effected by the use of disinfectants, which are substances which kill bacteria and their spores and also all animal parasites. Antiseptics are agents which inhibit



the growth of bacteria. In some cases bacteria and other lower organisms are killed by special means in such processes as brewing in order to prevent the formation of undesirable products by their action. Bacteria, which are minute unicellular organisms (*protophyta*) allied to plants, are the usual cause of infection (typhoid, tuberculosis, cholera), but sometimes unicellular animal organisms (*protozoa*) are the active agents (malaria, dysentery).

A distinction is made between *aerobic* bacteria, which require the presence of oxygen; *anaerobic* bacteria, which live only in the absence of free oxygen; and *facultative anaerobic* bacteria (the usual type), which occupy an intermediate position.

Physical methods of disinfection involve the use of heat, light, dryness, and radium. Sunlight has a particularly powerful effect: exposure for a few hours will generally kill bacteria. Ultra-violet light is also very active in sterilising transparent liquids, such as water; radium rays are active only in thin layers of material. Steam or 'moist' heat is much more effective than heating the dry materials: exposure for about 15 minutes to steam will kill bacteria, but their spores require longer. Cold is not effective: bacteria still live in materials at the temperature of liquid air, and the object of refrigeration is to check their development rather than to kill them.

Chemical disinfectants include ozone, chlorine (which is very active), sulphur dioxide (which is not very active and does not kill spores), hydrocyanic acid gas (mostly used in killing insects in fruit plantations), and formaldehyde, all used in the *gaseous* state; disinfectants used in *solution* include chlorine, hypochlorites (such as bleaching powder), iodine, acids (especially formic and hydrofluosilicic), permanganates, hydrogen peroxide, other peroxides, alkalies, soap, metallic salts, such as mercuric chloride (corrosive sublimate), mercuric iodide (biniodide of mercury), and salts of copper and silver, and many organic substances, such as alcohol (50-70 per cent.: weaker or stronger is much less active), formaldehyde ('formalin'), phenol ('carbolic acid'), and related substances such as cresols (found in certain tar fractions and more powerful than phenol), etc. The cresols are sparingly soluble and are emulsified, say with soap, for use, or else converted into soluble compounds, say by treatment with sulphuric acid. Most of the organic disinfectants have trade names ('Jeyes' fluid,' 'lysol,' etc., etc.).

The activity of a disinfectant is generally tested by comparing the action of solutions of it on an emulsion of typhoid bacilli with that of solutions of phenol (*Rideal-Walker test*).



The addition of ammonia to solutions of chlorine or hypochlorites increases their disinfecting power, owing to the formation of chloramine,  $\text{NH}_2\text{Cl}$ .

**Antibacterial drugs.**—Successful antibacterial drugs must destroy bacteria without injuring the delicate human tissues, and many substances which kill bacteria are too toxic for human use. The action of antibacterial agents may be *bactericidal*, when the bacteria are killed, or *bacteriostatic*, when the rapid growth of organisms is prevented, and the normal body-protective mechanism is given a chance to function successfully. Modern antibacterial drugs include the *sulphonamides* and *antibiotics*, which exhibit very little toxicity to the human body. They are primarily bacteriostatic, direct bactericidal effects not being possible with the concentrations of the drugs reached in the tissues.

The *sulphonamide drugs* are derivatives, or potential derivatives, of the compound *sulphanilamide*, having the formula  $\text{SO}_2\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , the two substituent groups being in the para-position (p. 522) in the benzene ring. There has been much research on this group since 1935, and the production of sulphanilamide is now very extensive. Over a thousand derivatives of it have been studied, and the products are used in treating a variety of infections, such as tonsillitis, pneumonia, meningitis, etc. The sulphonamides affect the normal intestinal bacteria which in some persons produce small amounts of the vitamin B complex.

The study of *antibiotics* was foreshadowed by Pasteur, who suggested that certain bacterial products should be effective in destroying other bacteria, a result called 'bacterial antagonism'. Antibacterial substances produced by moulds and bacteria are sometimes called antibiotics. Following the work of Fleming and Flory in England, a chemical substance called *penicillin* has been prepared in a state of purity. Penicillin is the sodium or calcium salt of an acid produced when *Penicillium notatum* or other related moulds are grown under appropriate conditions on or in a culture medium. When pure it is white solid, very soluble in water, containing 1666 unit doses per mg. It is made on the large scale. It must be stored at a temperature not above  $10^\circ$ . Penicillin is remarkable in being so non-toxic to the human body that relatively high concentrations could be maintained in the blood and tissues for several days, and yet at the same time is the most active bacteriostatic agent yet known against a number of deleterious organisms.

Besides penicillin, other antibiotics are known. *Streptomycin*, formed in *Actinomyces* fermentations, is said to have a curative action against some forms of tuberculosis.



## CHAPTER XXX

### THE METALS. THE ALKALI METALS

**\* Occurrence of metals.**—A few metals, *e.g.*, gold, platinum, and copper, sometimes occur as such and are then called **native**. In other cases the metals occur as compounds which are called **ores**. These are frequently oxides (*e.g.*, of iron and tin), carbonates (*e.g.*, of copper and iron), and sulphides (*e.g.*, of copper, zinc, lead and mercury). It does not follow that any compound of a metal which occurs abundantly is suitable for the extraction ('smelting' or 'winning') of the metal. For example, iron pyrites ( $\text{FeS}_2$ ) is not suitable for the smelting of iron and is not called an 'ore' of iron, although some iron is obtained from burnt pyrites left in sulphuric acid works (p. 361). The ores of metals are supposed to have been deposited, along with the gangue minerals (see below), from solutions of the materials of the primary rocks. The lower parts of the veins, not exposed to oxidation, contain sulphides, whilst the upper parts, exposed to water containing dissolved air percolating from the surface contain sulphates, carbonates, and oxides.

**\* Winning metals from ores.**—The method of extraction from the ore varies with the particular metal and the nature of the ore. Generally speaking, oxide ores are directly reduced by carbon to the metal; carbonates are first roasted in air to form the oxides, which are then reduced by carbon; sulphides are first roasted in air to the oxides, sulphur dioxide being evolved, and the oxides may be reduced with carbon, but special methods are sometimes used. Generally the ore contains rocky impurity, such as silica or silicates, called *gangue*. This is removed as far as possible by mechanical treatment and sometimes *flotation* (*q.v.*). To remove the gangue left with the ore, a *flux* is added, generally quicklime with or without fluorspar, during smelting. This combines with the silica to form a fusible mass, *e.g.*, of calcium silicate, called *slag*, which floats on the surface of the metal and is easily separated. The slag is generally glassy

but opaque in appearance when solid. Some slags are used as road material ('road metal') and others as fertilisers (p. 422).

Various types of furnace are used in metallurgy (the extraction of metals from ores): in some cases the temperature at which reduction occurs is so high that the electric furnace must be used. A few metals (*e.g.*, aluminium) are obtained by the electrolysis of fused salts or of solutions, and copper is *purified* in this way. Generally, however, a furnace fired with coke or coal is used, the combustion being effected either with natural draught, say by a chimney, or by forced blast.

**Metals and non-metals.**—The division of elements into metals and non-metals is convenient but somewhat arbitrary, because there are exceptions to most of the definitions of each. The following table represents the main features of difference, with the important exceptions:

#### I. PHYSICAL DIFFERENCES

Non-metals:	Metals
(1) have no lustre (except iodine and graphite);	(1) possess a lustre (except in powder form, although gold, bronze, and aluminium are lustrous even as powders);
(2) are not malleable;	(2) are malleable ( <i>i.e.</i> , can be hammered into sheets: some metals, <i>e.g.</i> , antimony and bismuth, are brittle and crush to powder);
(3) have no tenacity;	(3) have tenacity ( <i>i.e.</i> , in the form of wire they resist rupture);
(4) have low densities (below 5);	(4) have high densities (several exceptions: lithium has a density of only 0.53; sodium, potassium, magnesium, calcium, and aluminium have low densities);
(5) are poor conductors of heat;	(5) are good conductors of heat (some are not very good);
(6) are poor conductors of electricity (except graphite).	(6) are good conductors of electricity (bismuth and mercury are not very good).



Metals are crystalline : most of them crystallise in the regular system (cubes, octahedra, etc.). A mass of metal is usually a confused jumble of tiny crystals, but in some cases (bismuth, antimony) the crystals are large. A curiosity of great practical utility is the possibility of making rods or wires of metals consisting of one long crystal. The tungsten filaments in some electric lamps are composed of such single crystals of the metal.

The lustre of a metallic surface, developed by polishing, is thought to be due to a skin of amorphous material spread over a coarser crystalline aggregate, and covering over the small irregularities in the surface.

The electrical conductivity of a metal is due to the presence in it of mobile free electrons. If we consider the sodium chloride lattice (Fig. 142, p. 190) and imagine the chlorine atoms replaced by electrons and the sodium ions to remain, we obtain an idea of metallic sodium. On applying a potential difference the electrons move and carry the current.

## II. CHEMICAL DIFFERENCES

### Non-metals :

(1) form acidic oxides (*e.g.*,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ ) ; some oxides (*e.g.*,  $\text{N}_2\text{O}$ ) are not acidic ;

(2) form halogen compounds completely decomposed by water which are not true salts (*e.g.*,  $\text{PCl}_3$  ;  $\text{CCl}_4$  is an exception, as it is not decomposed by water) ;

(3) are electronegative elements (see p. 211) ; form anions or show hardly any electrochemical properties (*e.g.*, carbon) ;

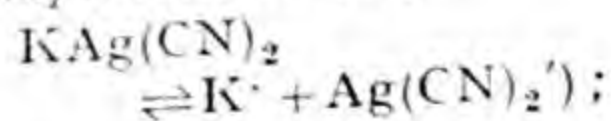
### Metals :

(1) normally form basic oxides (*e.g.*,  $\text{Na}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ), but some ( $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ), may act as feebly acidic oxides in presence of strong bases, and some metallic oxides of higher valency ( $\text{CrO}_3$ ,  $\text{Mn}_2\text{O}_7$ ) are acidic ;

(2) form halogen compounds stable in presence of water ( $\text{KCl}$ ,  $\text{PbCl}_2$ ) or decomposed only to a limited extent, the decomposition being reversed by excess of acid :



(3) are electropositive elements form cations (metals may sometimes form part of complex anions, *e.g.*,



II. CHEMICAL DIFFERENCES (*continued*)

Non-metals ( <i>continued</i> ):	Metals ( <i>continued</i> ):
(4) usually do not form complex salts.	(4) form complex salts in which the metal is sometimes present in the acid radical ( <i>anion</i> ) and sometimes in the basic radical ( <i>cation</i> ) ( <i>e.g.</i> , potassium ferrocyanide, $K_4FeC_6N_6$ gives ions $4K^+$ and $FeC_6N_6^{4-}$ ; silver ammonia chloride, $Ag(NH_3)_2Cl$ gives ions $Ag(NH_3)_2^+$ and $Cl^-$ ).

\* **Alloys.**—If two or more metals are fused together they usually, but not always (*e.g.*, zinc and lead do not mix except to a limited extent), form a homogeneous liquid, and the intimate association of the metals which is formed on solidification is called an alloy. The name alloy, which was used in this sense by Chaucer, is derived from the Latin *alligare*, mediaeval Latin *alloyare*, 'to bind to.' The preparation of alloys by fusion is the method most commonly used. The strong compression of finely-powdered metals, the simultaneous electro-deposition of the metals from a mixed solution (*e.g.*, copper and zinc, in the form of brass, from a solution of the cyanides in potassium cyanide), and the reduction of one or more of the metals from compounds in the presence of the other metal, are alternative processes leading to the formation of alloys. Alloys containing mercury are called **amalgams**, perhaps from the Arabic *al magma*, (Greek *migma*), a mixture.

It is only rarely that a solid alloy is homogeneous; usually the metals crystallise out separately or sometimes compounds of the metals (*e.g.*  $CuMg_2$ ,  $Zn_3Cu_2$ ,  $AlCu$ ) are formed and separate out, perhaps with the pure metals. The structure of the alloy may be coarse (Fig. 342) or fine (Fig. 343).

Many alloys contain solid solutions of two metals. These are homogeneous although solid, but are not definite chemical compounds, although solid solutions of the latter may be formed.

In nearly all cases one constituent separates before the others,



but sometimes a homogeneous alloy is formed by very rapid cooling (quenching). It is then usually hard and brittle, and an alloy before use generally requires heat treatment or annealing.



FIG. 342.—PHOTOMICROGRAPH OF A COARSE-STRUCTURE ALLOY.

The heterogeneous nature of some alloys is very valuable. **Antifriction metals** used for bearings for engine crankshafts, etc.,

contain hard particles embedded in a mass of soft metal. The hard particles bear most of the pressure, but as the bearing wears away they are kept from projecting from the mass and causing friction, since the soft matrix yields, and allows the harder parts to sink into the mass. These alloys generally have fairly low melting points and if a motor engine is raced when cold and before lubricant is flowing freely, or if lubricant fails, the bearings 'run,' *i.e.*, the alloy melts out. They have also no strength and require to be backed by other metals, such as bronze, and then carefully 'scraped'



FIG. 343.—PHOTOMICROGRAPH OF A FINE-STRUCTURE ALLOY.

as so to fit the moving part very exactly. A very tight fit is made in a new engine, and this requires 'running in.'

A brief general account of some useful alloys has been given in the introduction: a table of some important ones is given below:

Name of alloy:	Metals composing alloy:	Uses of alloy:
Bronze and gun-metal	Copper and tin	Coinage, statuary, tough parts of machinery
Brass	Copper and zinc	Sheets, tubes, ornaments.
Antifriction metal	Copper, tin, and antimony	Bearings
German silver	Copper, nickel, and zinc	Numerous
Stellite (very hard and non-corroding)	Chromium, tungsten, and cobalt	Surgical instruments
Stainless steel	Iron and chromium	Cutlery
Pewter and solder	Tin and lead	Vessels; soldering
Type metal	Lead, tin, and antimony	Printing type
Fusible metal	Lead, tin, bismuth, and cadmium	Safety sprinklers
Cobalt steel	Iron with 35 per cent. cobalt	Permanent magnets
Silicon steels	Iron and Silicon	Electromagnets (up to 4 per cent. Si); acid resisting alloys (up to 15 per cent. Si).

\* **Modern utilisation of metals.**—Our knowledge of the production and applications of metals has enormously increased in recent years. At the time when George Stephenson's locomotive, the 'Rocket,' was being built in 1829, not only was there no large commercial production of metals and alloys of the quality and type which we look upon as commonplace to-day, but the actual production was, to our present-day ideas, very small. The whole amount of cast iron produced in the world in 1850, before the invention of the Bessemer steel process, was only  $4\frac{1}{2}$  million tons, whilst in 1926 this had grown to over 77 million tons.



The amount of steel did not reach half a million tons per annum until 1870, whilst in 1926 it had grown to over 90 million tons. 'Steel' and 'iron' now include a great many varieties, used for special purposes. Stephenson's 'Rocket' was built from ordinary cast and wrought iron and a small amount of brass, whereas in a modern locomotive 32 different kinds of forged, wrought, and cast steels, 4 kinds of wrought iron, 3 kinds of malleable and cast iron, 12 kinds of brass and bronze, and 4 other metals are used, each being standardised by particular specifications. The engineer, in his calculations, must know exactly the properties of each kind of metal used. The British Standards Institution specifies over a hundred different classes of steel alone.

The valuable properties of certain special alloys of iron—so-called alloy steels (tungsten steel, silicon steel, and manganese steel)—have practically revolutionised some branches of engineering. The alloys of steel, notably those with chromium and nickel, have made possible the mechanical revolution which has taken place through the autocar and the aeroplane. Special nickel steels for very high-pressure boilers are also coming into use.

Some idea of the great advantages of alloy steels may be obtained from figures quoted by Sir Henry Fowler for the issue of chisels in the locomotive shops at Derby. The average number of old type carbon-steel chisels used per man per year was 18, whilst the number of modern nickel-steel chisels, of the same price, was 1·2.

Progress has by no means been confined to iron and steel. Aluminium was not known commercially until about 1890, and even in 1913 the world's production was only 64,000 tons. In 1926 this had risen to 235,000 tons. Special alloys of aluminium have most valuable properties, since they combine great strength with remarkable lightness. The specific gravity of *duralumin*, one of these alloys, is little more than one-third that of steel. Such alloys are widely used for aeronautical and other purposes, and for the pistons of internal combustion engines. Much use has also been made of magnesium alloys, which are even lighter than those of aluminium.

Many metals which until quite recently were regarded as 'rare' are now finding industrial applications. Cadmium (which is found in most zinc ores) is used for non-corrosive plating, as an alloy with copper for telephone and tramway cables, and in other alloys for solders and bearing metals.

Chromium is now used instead of nickel for plating ; it is very hard and does not corrode. Tungsten is used in metal filament electric lamps, and vanadium and molybdenum are used in special alloy steels. A knowledge of the chemistry of the 'important' metals only, which was once sufficient for the chemist, is now too narrow, since many of the so-called 'rare metals' may occur in products used in everyday life. In a book of this kind it is possible to mention these only very briefly.

#### THE ALKALI METALS : SODIUM AND POTASSIUM

**The alkalies.**—It is usual to commence the study of the metallic elements with the common alkali metals, sodium and potassium, although these metals were not discovered until the beginning of the nineteenth century and are rarely seen except in the laboratory, whereas copper, gold, silver, and some other metals have been known for about 6,000 years. The compounds of the alkali metals, however, have been known and used for a very long time, and their chemistry is simple, since these elements form only one series of compounds, whereas both copper and iron give two distinct series of compounds, the study of which is more difficult. There is, therefore, much to be said in favour of retaining the traditional course of treatment.

Wood ashes and *natron* (from lakes in Egypt) were used in antiquity as *detergents*, i.e., for washing clothes, but there was no clear distinction made between them. The Arabs called the salt (potassium carbonate) extracted from wood ashes by water, *al qali*, from which the name alkali is derived. Natron (sodium carbonate, which the Romans called *nitrum*, incorrectly translated 'nitre' in the Authorised Version of the Bible) was later obtained from the ashes (*barilla*) of plants growing on the sea-shore, and was called the *marine alkali*, that from wood ashes being called the *vegetable alkali*. Marggraf in 1757 first clearly distinguished between the two. The *volatile alkali* (ammonium carbonate) was obtained by the dry distillation of bones, horns, and animal matter.

It was discovered in the Roman period, probably in Egypt, that when solutions of the natural alkalies are boiled with quicklime slaked with water, they become very corrosive and *caustic*, and the names *caustic potash* and *caustic soda* were later used for the products. Galen refers to the causticising of alkali for making soap. Alkalies are largely used in making washing powders, soaps, and glass (*q.v.*).



**Black's researches on the alkalies.**—The chemical nature of the alkalies was largely elucidated by the classical researches of Joseph Black (1728-1799), (*Dissertation on Magnesia*, 1754). In his time three alkalies, and a mild and caustic form of each,



FIG. 344.—JOSEPH BLACK, 1728-1799.

were known ; viz. the vegetable alkali, the marine alkali, and the volatile alkali (the caustic form of which was first described by Boyle in 1675).

According to the theory then in vogue, limestone on burning absorbs a 'principle of causticity' from the fire, which imparts its properties to the quicklime. The process of converting a mild into a caustic alkali by boiling with quicklime was regarded as due to the transfer of the 'principle of causticity' from the quicklime to the mild alkali.

Black studied the subject quantitatively, using the balance, and found that when limestone is heated there is a loss in weight and fixed air (gaseous carbon dioxide, entirely overlooked in the previous scheme) is evolved. The residue is quick-lime :

$$(1) \quad \text{limestone} = \text{quicklime} + \text{fixed air.}$$

The quicklime was then boiled with a solution of mild alkali. The alkali became caustic, and the quicklime was reconverted into the original weight of limestone :

$$(2) \quad \text{quicklime} + \text{mild alkali} = \text{limestone} + \text{caustic alkali}$$

If we add equation (1) to equation (2) we find :

$$\text{mild alkali} = \text{caustic alkali} + \text{fixed air,}$$

so that the corrosiveness of quicklime and caustic alkali is 'an essential property of the pure earth' and the pure alkali, respectively, and is not due to any separate 'principle of causticity.'

Black also remarked that fixed air is given off by the action of acids on both limestone and mild alkali : 'when we mix an acid with an alkali, or with an absorbent earth (limestone or chalk), the air is set at liberty and breaks out with violence ; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time.' When the solution of limestone in acid is mixed with mild alkali, the original weight of limestone is precipitated. In this case no fixed air is evolved from the mild alkali, although the latter forms a salt with the acid. This is because the fixed air is transferred to the lime, with the formation of limestone.

The theory of caustification is thus stated by Black : 'If quicklime be mixed with a dissolved alkali, it likewise shows an attraction for fixed air, superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself ; while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony, or strong attraction for water, and for bodies of the inflammable, and of the animal and vegetable kind ; which attraction was less perceivable, as long as it was saturated with air. And the volatile alkali, when deprived of its air, besides this attraction for various bodies, discovers likewise its natural degree of volatility, which was formerly somewhat



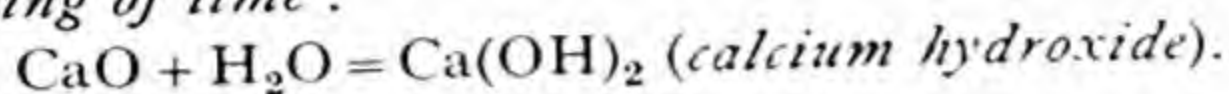
repressed, by the air adhering to it, in the same manner as it is repressed by the addition of an acid.'

The reactions involved in the processes studied by Black can be represented by the following equations of modern chemistry :

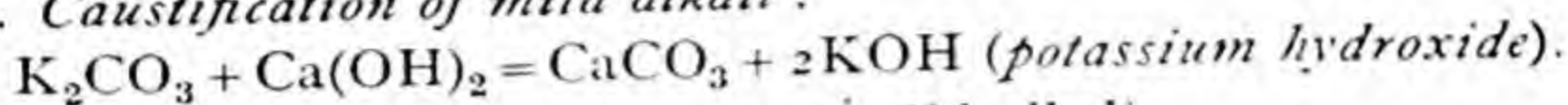
1. *Preparation of quicklime from limestone :*



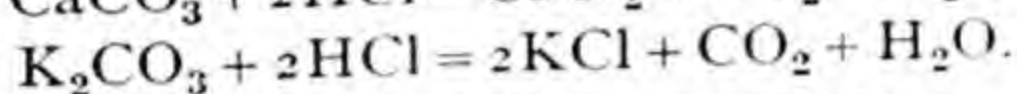
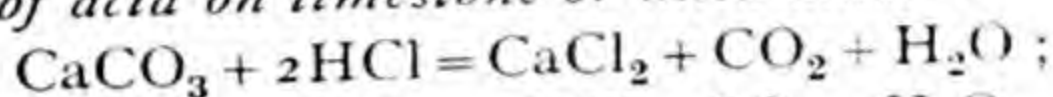
2. *Slaking of lime :*



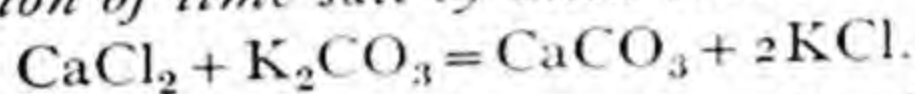
3. *Caustification of mild alkali :*



4. *Action of acid on limestone or mild alkali :*



5. *Precipitation of lime salt by mild alkali :*



**Davy's isolation of the alkali metals.**—Previous to the researches of Davy the caustic alkalies were regarded as elements, although Lavoisier hinted that alkaline earths might be oxides of unknown metals. Humphry Davy (1778-1829), whose name is chiefly remembered for the invention of the safety lamp, carried out the earliest investigations on electrochemistry. Becoming convinced of the great power of decomposition exhibited by the voltaic battery, and attracted by Lavoisier's conjecture, Davy attempted to decompose the alkalies by electrolysis. The experiment succeeded.

In 1807 he found that : 'A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface (by attraction of moisture, and slight deliquescence), was placed upon an insulated disc of platina, connected with the negative side of the battery . . . in a state of intense activity ; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. . . . The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface ; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered with

a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash.'

This metal, which Davy called **potassium**, was found to possess extraordinary properties :

(1) It is lighter than water.

(2) When thrown on water it instantly decomposes it, attracting the oxygen ; the liberated hydrogen is ignited by the heat developed, and burns over the rapidly-moving floating globule of metal with a heliotrope-coloured flame. A solution of caustic potash is formed.

(3) The metal rapidly oxidises in the air ; a freshly-cut piece, which shows a bright, metallic lustre for an instant, becoming at once covered with a blue tarnish. The metal is therefore preserved under petroleum, which is free from oxygen.

The metal **sodium** was also isolated from caustic soda by electrolysis. Sodium, like potassium, decomposes water, but, as the heat evolution is not so great, the liberated hydrogen does not take fire unless the sodium is prevented from moving about by placing it on starch-jelly ; the hydrogen then catches fire, and burns with a bright yellow flame.

Gay-Lussac and Thenard in 1808 showed that, when molten caustic potash or soda was brought in contact with red-hot iron turnings, the iron was oxidised, and the alkali metal distilled off. At the same time, a considerable amount of hydrogen was evolved. The caustic alkalies were then recognised as **hydroxides**, KOH and NaOH, of the metals potassium and sodium.

The presence of hydrogen in caustic potash or soda may be shown by heating a mixture of the powdered alkali with iron filings in a hard glass tube. Hydrogen is evolved, and may be ignited at the mouth of the tube.

**The Leblanc alkali industry.**—Sodium carbonate in a very impure form was formerly prepared by burning plants growing on the seashore. The plant-ash (*barilla*) was used in the manufacture of glass and soap.

Large quantities of natural sodium carbonate occur in some lakes, e.g., Lake Magadi, in British East Africa, is estimated to contain 200,000,000 tons of sodium carbonate and the latter is produced technically from it. It was obtained in antiquity from Egyptian lakes.

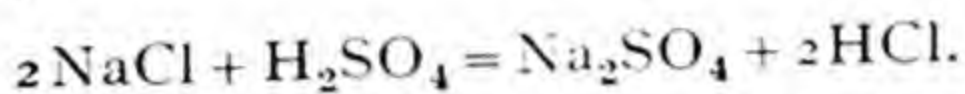
When Stahl pointed out that common salt is a compound of soda, many attempts were made to obtain the alkali from it,



but the first really satisfactory method was devised by Nicolas Leblanc in 1787, as a result of an offer of a prize by the French Academy for a solution of the problem. Leblanc established his process in a works by means of a loan from the Duke of Orleans in 1791. Two years later the Duke was guillotined and Leblanc's factory was confiscated. The unfortunate inventor, who indeed escaped the fate of his benefactor, lingered on only to die by his own hand in 1806.

After the repeal of the salt tax in England, an alkali works was established in Lancashire, in 1823, by Muspratt, in which the **Leblanc process** was used, and during the nineteenth century the method was everywhere in use. The process comprised the following steps :

(1) Salt is converted into sodium sulphate by heating with sulphuric acid :



The process was carried out in two stages as described on p. 320, the hydrochloric acid being absorbed in water.

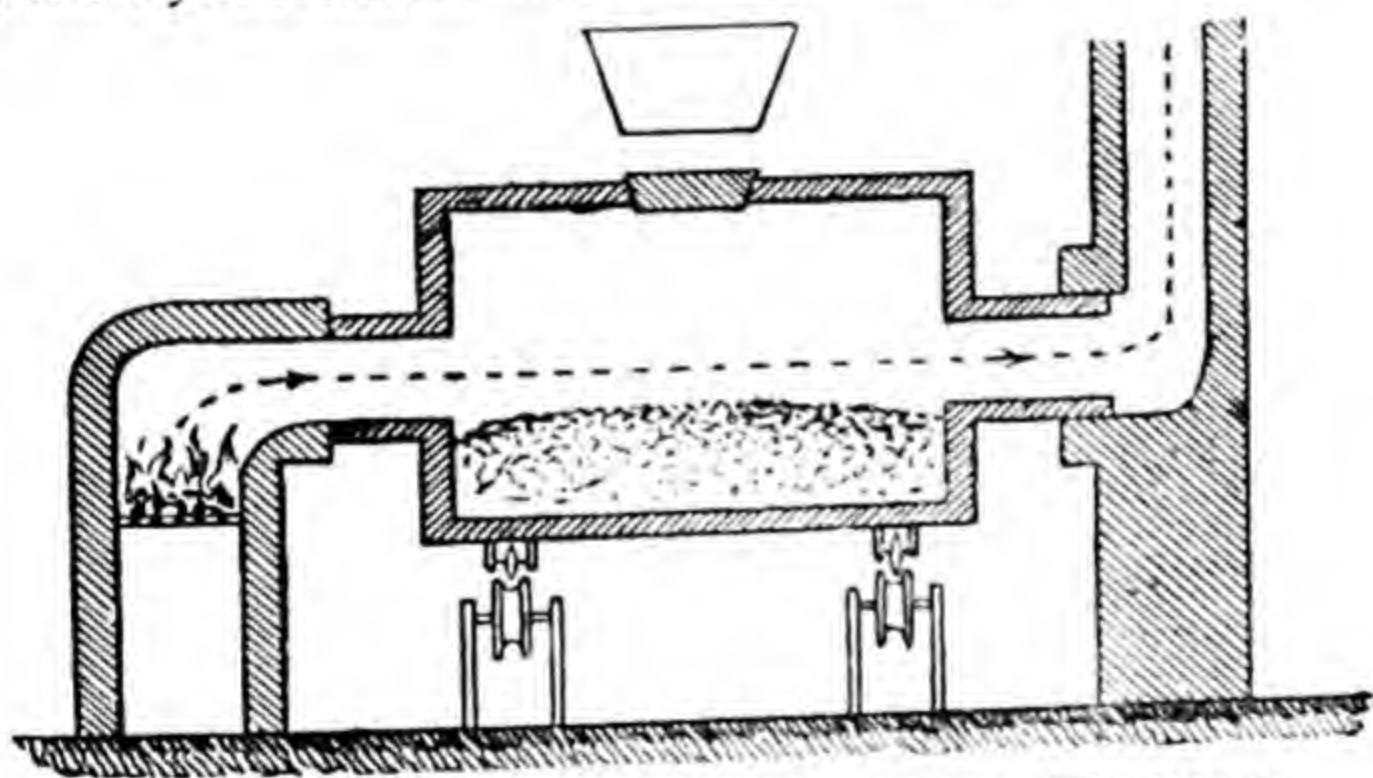
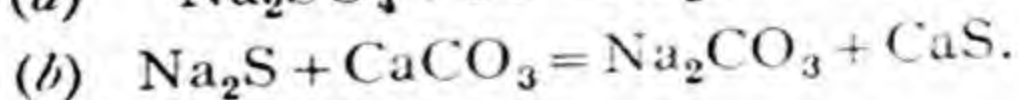
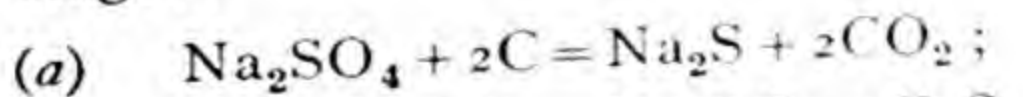


FIG. 345.—BLACK ASH REVOLVING FURNACE.

(2) The sodium sulphate, or *salt-cake*, is heated to dull redness with limestone and powdered coal in a large revolving furnace by flames from a gas-producer (Fig. 345), when sodium carbonate and calcium sulphide are produced. The reaction occurs in two stages :



The final product is known as *black-ash*; if it is broken up and lixiviated with water, an impure solution of sodium carbonate is obtained which can be crystallised, whilst the sparingly soluble calcium sulphide (with excess of coal, limestone, and impurities) remains as *alkali waste*.

The Leblanc process was very suitable for development in Great Britain, since the three raw materials, *salt*, *coal*, and *limestone* occur in the island in abundance. The sulphuric acid was manufactured from imported pyrites, but much of the sulphur, was, in later years, extracted from the alkali waste

(p. 343). The hydrochloric acid obtained as a secondary product was used in the manufacture of chlorine and bleaching powder. From the pyrites cinders, copper was extracted, since those kinds of pyrites which contain copper were selected for use. It will be seen that a number of important industries were linked together by the Leblanc process, and during the nineteenth century it was one of the most important British industries, the production of sodium carbonate in the period 1879-1883 being half a million tons per annum. About 1924 the Leblanc process became obsolete in Great Britain, and the soda and

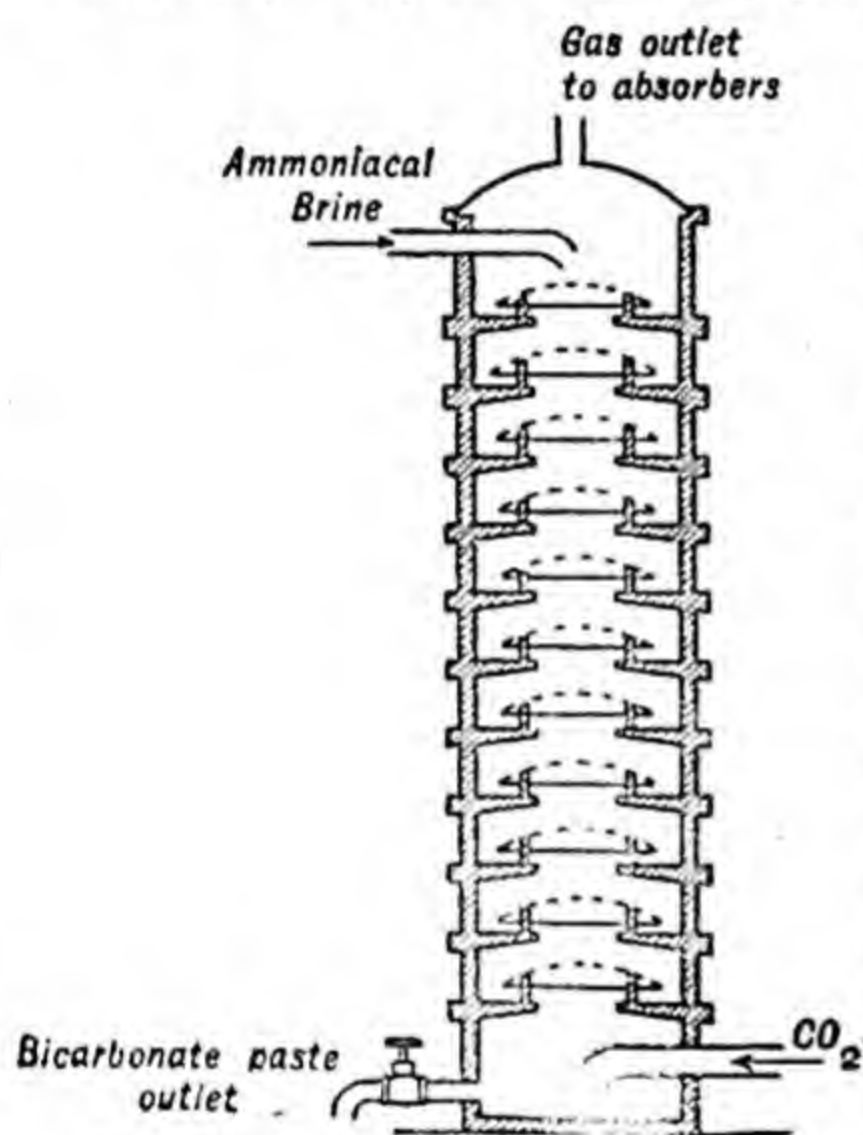


FIG. 346.—CARBONATING TOWER;  
AMMONIA-SODA PROCESS.

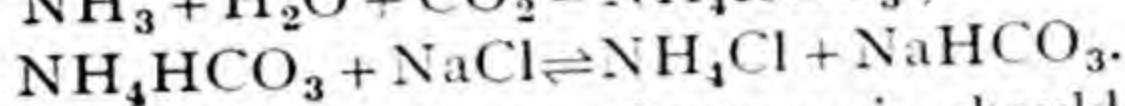
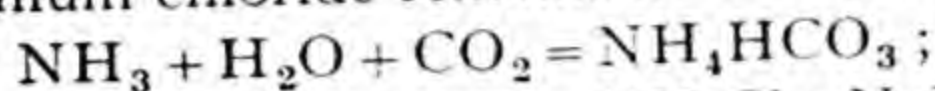
chlorine formerly made by it are now manufactured by electrolytic methods (p. 315).

**The ammonia-soda process.**—About the middle of the nineteenth century another process for the manufacture of soda gradually became a serious rival of the Leblanc process, viz. the **ammonia-soda process**, which was at first worked alongside the old process and then largely displaced it. It was patented in England by Dyar and Hemming in 1838, was first operated on a technical scale by Schloesing and Rolland in France from 1855, but was so much improved by Ernest Solvay of Brussels, about ten years later, that it is sometimes called the Solvay process. It was, however, first worked really successfully near Northwich on

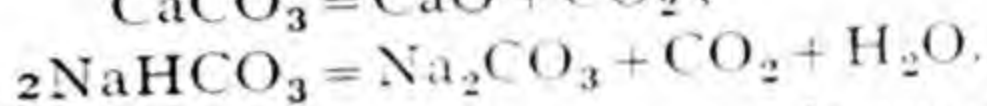
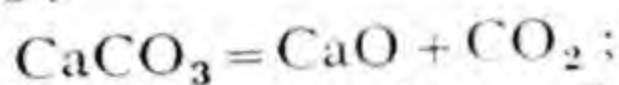


the Cheshire brinefields by John Brunner and Dr. Ludwig Mond ; it is still operated there, and in Europe and America.

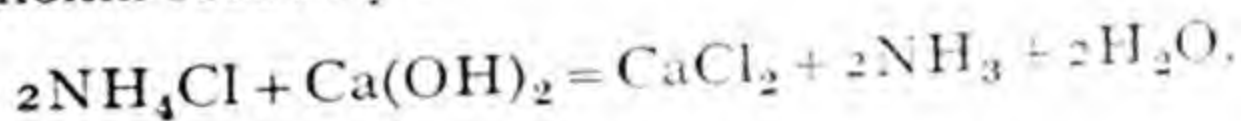
In the ammonia-soda process, ammonia gas is dissolved in the brine, nearly saturated with salt, and carbon dioxide is passed in under pressure in **carbonating towers** (Fig. 346), an invention of Solvay. Ammonium bicarbonate is formed and then reacts with the salt ; sodium bicarbonate is precipitated and ammonium chloride remains in solution :



It is essential that all waste of ammonia should be avoided. The ammonium chloride is decomposed by lime to set free the ammonia, which is used again and again, some being added to make up loss. The carbon dioxide evolved in making the quicklime from limestone and that formed in calcining the sodium bicarbonate to form sodium carbonate (*soda ash*) are used in the process :



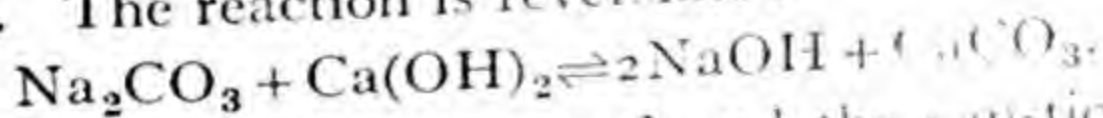
Only about two-thirds of the common salt are converted into bicarbonate since the reaction is reversible and leads to an equilibrium ; the rest is wasted, and the calcium chloride formed in the ammonia recovery :



cannot all be used.

From soda ash various products are made. Washing soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , is obtained in large efflorescent crystals, easily soluble in water, by dissolving soda-ash in hot water and crystallising. **Crystal carbonate**,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , is formed by evaporation, and separates from the hot solution. Concentrated soda **crystals**,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , are produced by crystallising a hot solution of equimolecular amounts of carbonate and bicarbonate.

**Sodium hydroxide.**—Sodium hydroxide, or caustic soda,  $\text{NaOH}$ , is made by boiling a solution of sodium carbonate with slaked lime. The reaction is reversible :



The filtered solution is evaporated and the caustic soda fused in iron pans. It may be cast into sticks or coarsely powdered.

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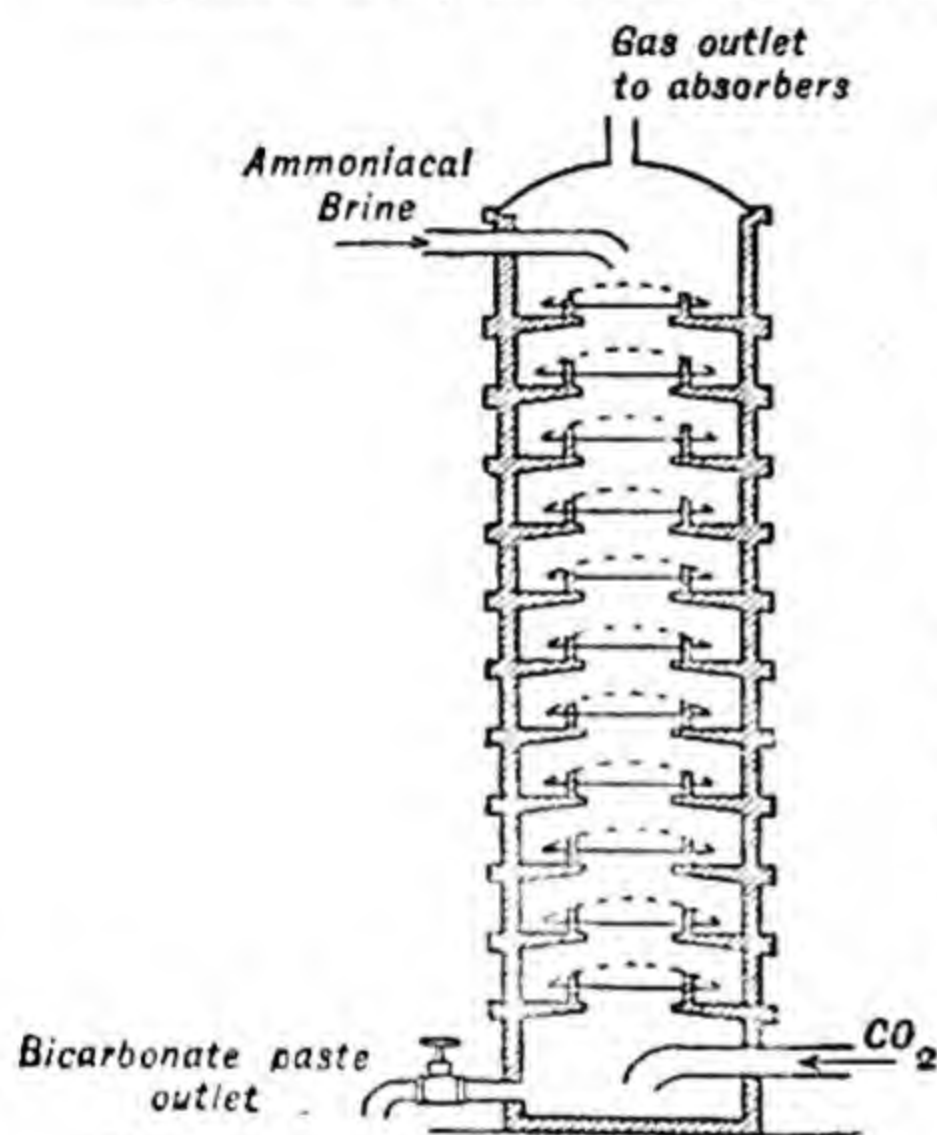


FIG. 346.—CARBONATING TOWER:  
AMMONIA-SODA PROCESS.

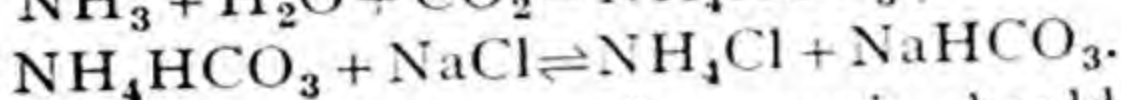
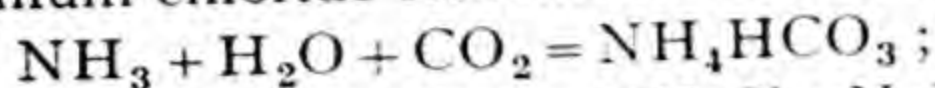
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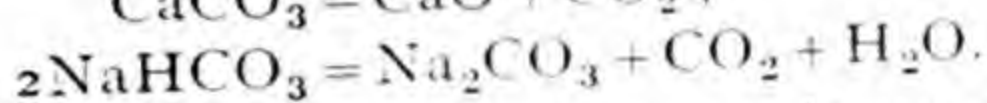
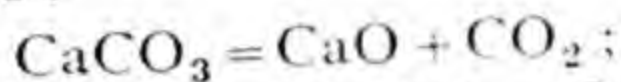


the Cheshire brinefields by John Brunner and Dr. Ludwig Mond ; it is still operated there, and in Europe and America.

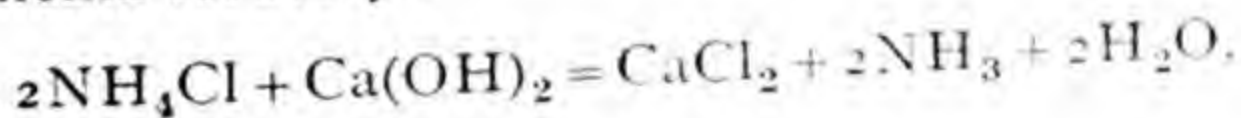
In the ammonia-soda process, ammonia gas is dissolved in the brine, nearly saturated with salt, and carbon dioxide is passed in under pressure in **carbonating towers** (Fig. 346), an invention of Solvay. Ammonium bicarbonate is formed and then reacts with the salt ; sodium bicarbonate is precipitated and ammonium chloride remains in solution :



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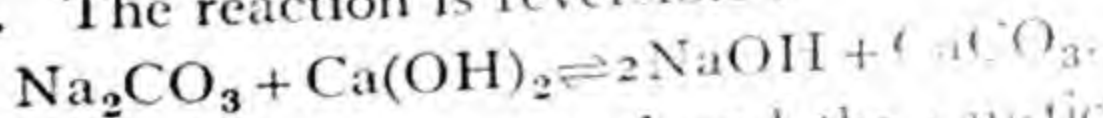
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**Sodium hydroxide.**—Sodium hydroxide, or caustic soda,  $\text{NaOH}$ , is made by boiling a solution of sodium carbonate with slaked lime. The reaction is reversible :

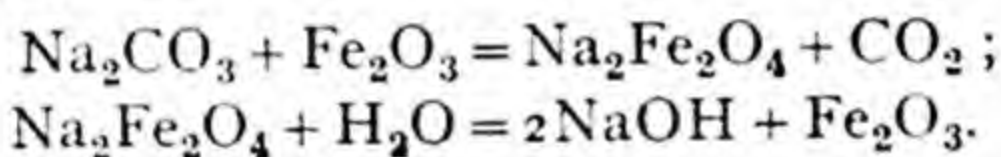


The filtered solution is evaporated and the caustic soda fused in iron pans. It may be cast into sticks or coarsely powdered.

Increasing amounts of caustic soda are now made directly from common salt by electrolytic processes (p. 315).

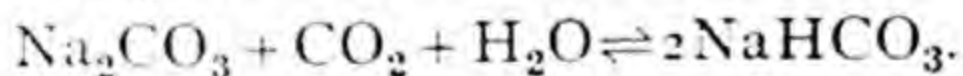
Caustic soda is a white, slightly translucent, fusible solid with a fibrous texture. When exposed to the air, it first deliquesces from absorption of moisture and a little carbon dioxide, forming a saturated solution. The latter, however, slowly resolidifies from absorption of more carbon dioxide, when sodium carbonate is formed, which is only sparingly soluble in caustic soda solution. (Caustic potash does *not* resolidify, since potassium carbonate is readily soluble. For this reason a concentrated solution of caustic potash is used to absorb carbon dioxide, since it does not deposit solid, which would choke the apparatus.) Caustic soda is a powerful caustery, breaking down the proteins of the skin and flesh to a pasty mass. Caustic soda and caustic potash in solution slowly attack and corrode glass. They should be evaporated in silver, nickel, or iron dishes.

Caustic soda was formerly made in Solvay works by heating soda ash with ferric oxide and decomposing the sodium ferrite with hot water :



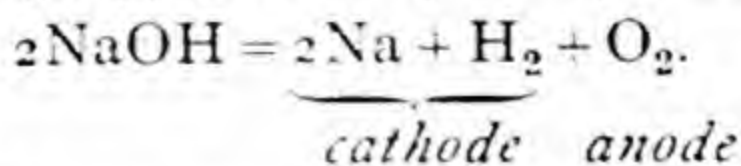
This is known as the **Löwig process**.

**Sodium bicarbonate.**—This salt, which is much less soluble than the normal carbonate and has much milder alkaline properties, is produced in large quantities by the ammonia-soda process, but is all converted into carbonate, the bicarbonate of commerce being prepared from the latter. A concentrated solution, or moist crystals, of sodium carbonate give, when saturated with carbon dioxide, a white crystalline precipitate of bicarbonate. This may be washed with a little cold water, in which it is sparingly soluble, and dried in the air :



Sodium bicarbonate is used as a mild alkali in medicine for removing acidity, and in making baking-powder (*q.v.*).

**Metallic sodium.**—The metal sodium is prepared by Davy's electrolytic process (p. 571) as adapted by Castner (1890) :

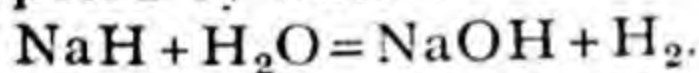


Caustic soda is fused in an iron pot and electrolysed by a cylindrical iron cathode and a nickel anode, separated by a wire



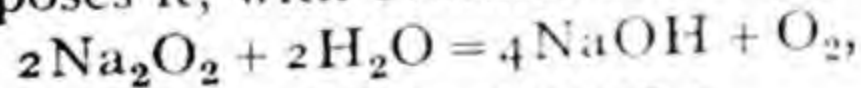
gauze cylinder (Fig. 347). The metal floats and is skimmed off. It is sold in the form of thick rods sealed up in tin cans. In the laboratory it is kept, like potassium, under petroleum, which excludes oxygen from the metal. Sodium is chiefly used for the manufacture of sodium cyanide ( $\text{NaCN}$ ) for the extraction of gold, and sodium peroxide, although it has other minor uses. It is a soft, silver-white metal, violently attacked by water, and is a good conductor of electricity (about one-third the conductivity of silver, the best conductor).

The metal forms a compound, sodium hydride,  $\text{NaH}$ , when heated in hydrogen; this is a colourless, salt-like solid decomposed by water:

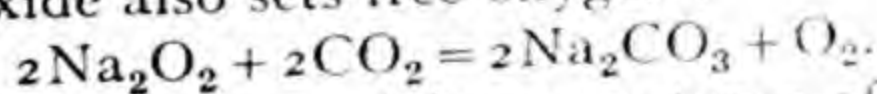


**Oxides of sodium.**—Two oxides of sodium are known: sodium monoxide,  $\text{Na}_2\text{O}$ , a basic oxide, and sodium peroxide,  $\text{Na}_2\text{O}_2$ , or  $\text{Na.O.O.Na}$ . Sodium monoxide is obtained by burning sodium in a limited supply of air. Sodium peroxide is produced when the metal burns in excess of air or oxygen, and is manufactured by heating sodium in aluminium trays in a current of purified air in iron pipes. Sodium peroxide is a yellow substance, becoming white on exposure to air from formation of sodium hydroxide and carbonate.

Water decomposes it, with evolution of oxygen:



and carbon dioxide also sets free oxygen:



Hence the peroxide is used in some types of diving helmets which do not require the supply of air. It is also used in bleaching (p. 325), since with *cold* water it is decomposed with formation of hydrogen peroxide:

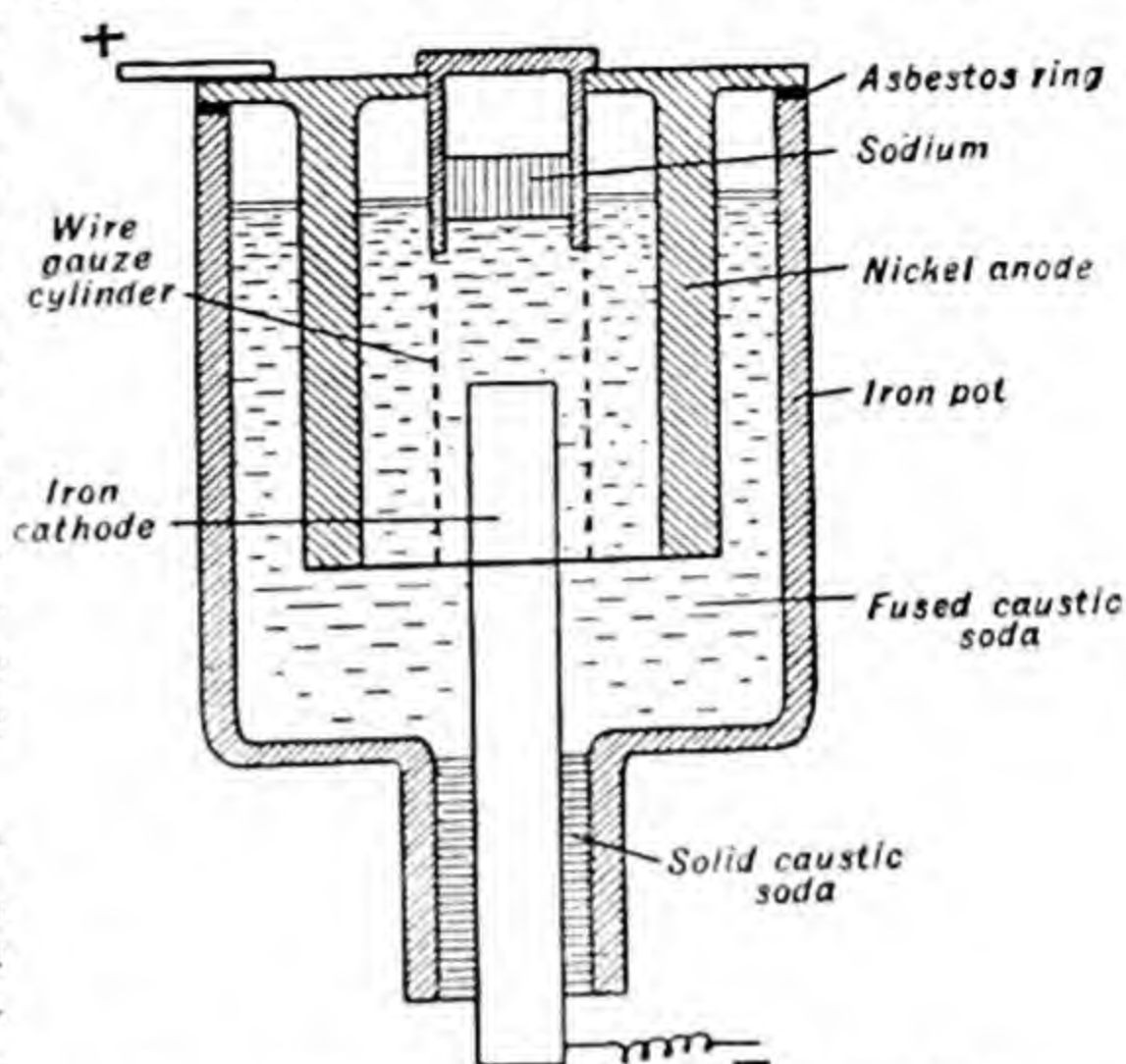
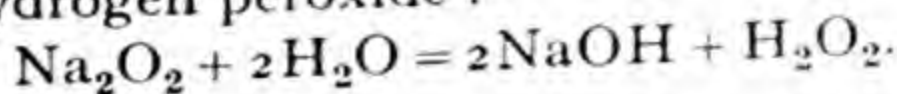


FIG. 347.—TECHNICAL PREPARATION OF SODIUM.

**Sodium sulphate.**—This salt,  $\text{Na}_2\text{SO}_4$ , is produced by the salt cake process (p. 573) and is used in making glass (p. 592). When crystallised from water it yields Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . The crystals of Glauber's salt melt at  $32^\circ$ , giving a saturated solution and depositing a white powder of anhydrous  $\text{Na}_2\text{SO}_4$ . Sodium hydrogen sulphate,  $\text{NaHSO}_4$ , is obtained by the action of sulphuric acid on the normal sulphate and as a by-product in the manufacture of nitric acid (p. 388). The pyrosulphate,  $\text{Na}_2\text{S}_2\text{O}_7$ , is obtained from it by gentle ignition. At a red heat the pyrosulphate decomposes into the normal sulphate and sulphur trioxide (p. 355).

### POTASSIUM

**Potassium compounds.**—Potassium occurs much less accessibly than sodium, although it is widely distributed throughout the three kingdoms of Nature. Primary rocks often contain potassium silicate; thus granite contains *felspar*:  $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$ . During the weathering of these rocks, *i.e.*, their decomposition by atmospheric carbon dioxide and water, assisted by the disintegrating action of frost, the silicates are decomposed into clay and soluble potassium salts, such as potassium carbonate. The latter are retained by a process of adsorption in the soil, where they remain available for absorption by the roots of plants (p. 422).

In plants, potassium compounds occur as salts of organic acids: *e.g.*, acid potassium oxalate, 'salt of sorrel,' or 'salts of lemon'; and acid potassium tartrate, 'cream of tartar,' or 'argol.' When plants are burnt, these organic salts form potassium carbonate,  $\text{K}_2\text{CO}_3$ , which, since it was formerly prepared by calcining cream of tartar, received the name *salt of tartar*. Large amounts of potassium carbonate are made by lixiviating wood ashes with water, evaporating the solution to dryness, and calcining the residue in iron pots. The product is *pot-ash*; when purified it is known as *pearl ash*. Sugar beets absorb from the soil considerable amounts of potassium salts, which accumulate in the residues, known as *vinasse*, or *schlempe*. They are burnt, leaving a residue of potassium carbonate.

Plants serve as food for animals, and the blood serum of all animals contains potassium and sodium. In the milk of carnivora, sodium and potassium occur in approximately equivalent amounts; in that of herbivora, and in human milk, potassium predominates. The perspiration of the sheep is rich in organic



potassium salts. If raw wool is washed with water, the brown liquid evaporated, and the residue calcined, potassium carbonate remains.

Potassium salts occur in the sea, and are absorbed in marine plants, from the ashes of which (*kelp*) they may be extracted.

**Deposits of potassium salts.**—Although potassium salts are widely distributed, comparatively few workable deposits occur. The principal are found at Stassfurt, in Saxony, and at Mulhouse, in Alsace.

The Stassfurt potash deposits held, until recently, the monopoly of the world's supply. They were discovered in boring for rocksalt in 1839, and are of great thickness. The deposits are probably derived from the evaporation of an inland lake, as the order of the successive layers of salts is what would be expected in such a case (Fig. 348).

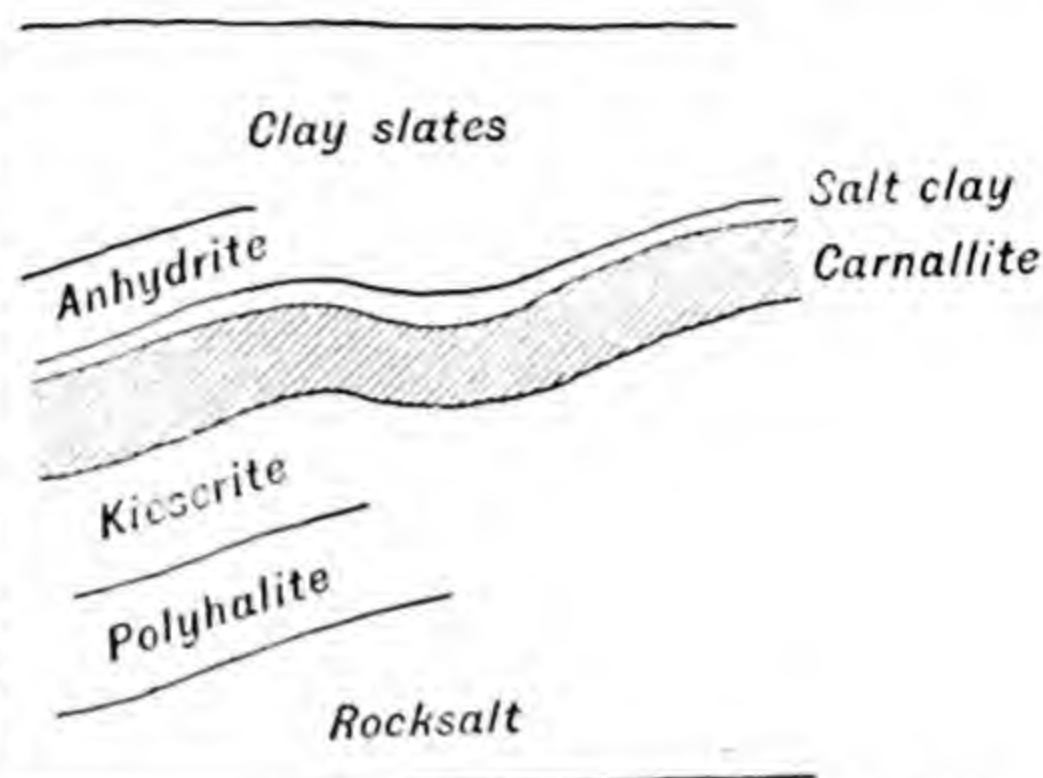


FIG. 348.—SECTION OF STASSFURT SALT DEPOSITS.

The chief source of potassium salts in the Stassfurt deposit is the double salt **carnallite**,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The Alsatian, and Galician, deposits contain *sylnite*, an isomorphous mixture of sodium and potassium chlorides, richer in potassium than carnallite.

**Potassium chloride** is obtained from carnallite by decomposing the salt with hot water and crystallising. The magnesium chloride, which is more soluble, is a useful by-product. Potassium salts are chiefly used as fertilisers, in making flint glass and hard glass (p. 592), soft soap (p. 520), and (as nitre) for gunpowder (p. 524).

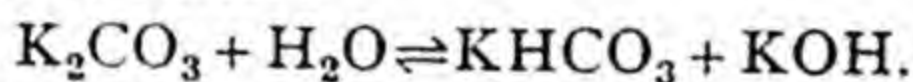
**Potassium.**—Metallic potassium is prepared in a similar way to sodium, viz. by the electrolysis of fused caustic potash. It comes into the market in small spheres, preserved under petroleum, and is a very soft metal, with a silver-white colour, not acted upon by perfectly dry oxygen, but rapidly corroded in moist air, becoming covered at first with a blue film. It acts violently on water, the liberated hydrogen burning with a purple

flame (p. 572). When heated with practically every gas containing oxygen, it abstracts the latter; it also decomposes boron oxide, silica, and the chlorides of magnesium and aluminium, on heating, with liberation of the elements. An alloy of potassium and sodium is liquid, like mercury, at room temperature. The vapour of potassium is green: that of sodium is violet.

**Oxides of potassium.**—Potassium monoxide,  $K_2O$ , is prepared in a similar manner to  $Na_2O$ , and has similar properties. Potassium dioxide,  $KO_2$ , is obtained as a chrome-yellow solid by burning the metal in oxygen or air (*cf.*  $Na_2O_2$ ).

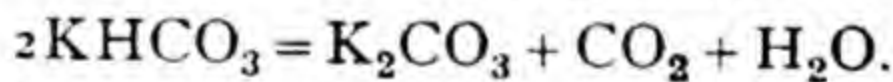
**Potassium hydroxide, or caustic potash.**—Caustic potash,  $KOH$ , is prepared in a similar manner to caustic soda, which it resembles closely in its properties. It is made on the large scale by the electrolysis of a solution of potassium chloride, and is used in the manufacture of soft-soap (p. 520).

**Potassium carbonate.**—Potassium carbonate,  $K_2CO_3$ , is a white deliquescent powder, dissolving readily in water to form a strongly alkaline solution:



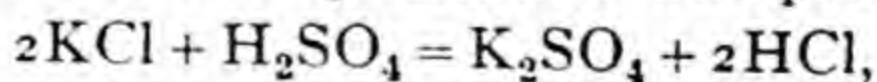
It is a fusible salt, but melts at a lower temperature when mixed with sodium carbonate, forming *fusion mixture*, which is used in the laboratory.

Moist potassium carbonate readily absorbs carbon dioxide, forming potassium hydrogen carbonate, or 'potassium bicarbonate,'  $KHCO_3$ , which is much less soluble in water than the normal carbonate and has milder alkaline properties. On heating, it gives off steam and carbon dioxide and leaves the normal carbonate:



Potassium carbonate is made from wood ashes or beet sugar residues (p. 493) or from the chloride by a method similar to the Leblanc process (p. 573: the ammonia process cannot be used, as  $KHCO_3$  is too soluble).

**Potassium sulphate.**—Potassium sulphate,  $K_2SO_4$ , is prepared by heating concentrated sulphuric acid with potassium chloride:



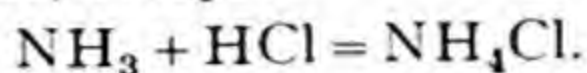
and is also extracted from Stassfurt salts, *e.g.*, *schönite*,  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ . It crystallises anhydrous, and is used as a fertiliser, especially for tobacco, since it has a higher melting point than potassium chloride (the commonest potassium fertiliser), and the ash of the tobacco is thus not so fusible. The



salts  $\text{KHSO}_4$  and  $\text{K}_2\text{S}_2\text{O}_7$  are prepared in the same way as  $\text{NaHSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_7$ .

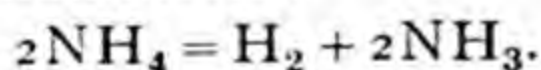
### AMMONIUM ( $\text{NH}_4$ )

**Ammonium compounds.**—Ammonia,  $\text{NH}_3$ , readily combines with acids to form salt-like compounds. If a jar of hydrogen chloride is inverted over one of ammonia gas, dense white fumes are produced which settle on the sides of the jars as solid flakes of *sal ammoniac*,  $\text{NH}_4\text{Cl}$ :

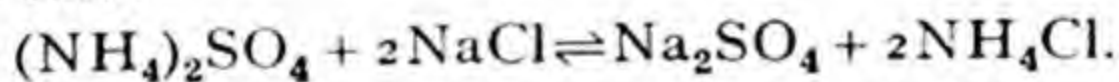


Davy in 1808 suggested that *sal ammoniac*, which resembles common salt in many of its properties, contains the positive radical **ammonium**,  $\text{NH}_4$ , analogous to an alkali metal. The ammonium salts really contain the **ammonium ion**,  $\text{NH}_4^+$ , analogous to the potassium and sodium ions. A solution of ammonia in water contains **ammonium hydroxide**,  $\text{NH}_4^+ + \text{OH}^-$ .

When sodium amalgam is put into a concentrated solution of ammonium chloride it swells up, and a soft, buttery mass is formed, which rapidly decomposes, evolving hydrogen and ammonia in the ratio  $\text{H}_2 : 2\text{NH}_3$ . Davy suggested that the product of the first reaction is an amalgam of **ammonium**, which is behaving like an alkali metal:



**Ammonium chloride.**—This compound,  $\text{NH}_4\text{Cl}$ , known as *sal ammoniac*, is prepared by neutralising ammonia solution with hydrochloric acid and evaporating. It is also made by boiling a solution of ammonium sulphate with an equivalent amount of common salt:



The sodium sulphate separates, and is removed: on cooling, ammonium chloride crystallises. It is purified by sublimation, by heating the salt in a cast-iron basin provided with an iron dome, having a small hole at the top. The cake of ammonium chloride which sublimes into the dome is broken up, and forms tough, fibrous lumps. A mixture of ammonium sulphate and common salt may also be heated in the same apparatus. An imitation of the sublimed product is made by strongly compressing the powdered salt: *voltaids*, used in batteries, are small tablets prepared by compression. Ammonium chloride is prepared in ammonia-soda works by crystallising the liquors from the bicarbonate filters (p. 575).

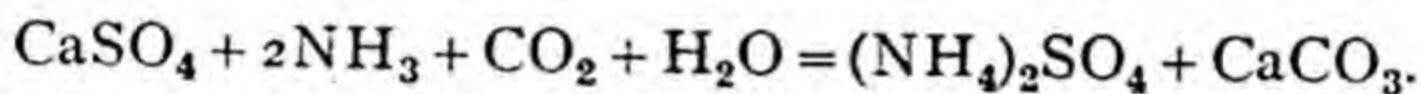
The salt is readily soluble in water, and a considerable lowering of temperature results.

The *vapour* of ammonium chloride is dissociated (p. 164) :



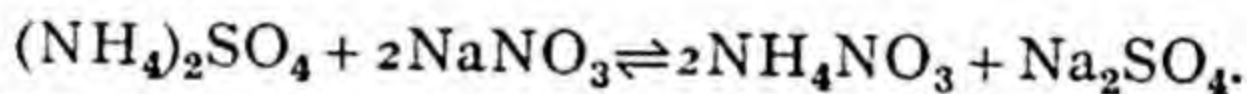
The ready dissociation of the salt on heating explains its action as a *flux* in soldering: the oxides are converted into volatile chlorides by the hydrochloric acid, and a clean metal surface is left.

**Ammonium sulphate.**—This important salt,  $(\text{NH}_4)_2\text{SO}_4$ , is made by absorbing ammonia in diluted sulphuric acid (p. 380). Instead of using sulphuric acid as absorbent, ammonia may be passed into a suspension of calcium sulphate (calcined gypsum), carbon dioxide being also passed through the liquid. Calcium carbonate is precipitated, and a solution of ammonium sulphate is formed :



Ammonium sulphate forms crystals isomorphous with potassium sulphate, and very soluble in water. It is used as a fertiliser.

**Ammonium nitrate.**—This salt,  $\text{NH}_4\text{NO}_3$ , was first prepared by Glauber, and was called *nitrum flammans*, since on strong heating it decomposes violently, with production of flame. It is obtained by neutralising nitric acid with ammonia or ammonium carbonate, or by the double decomposition of ammonium sulphate and sodium nitrate :



It is used in the preparation of nitrous oxide gas (p. 394) and in making explosives (p. 527).

**Ammonium carbonate.**—The commercial ammonium carbonate, which is formed by subliming a mixture of ammonium chloride and chalk, or by the reaction between ammonia, water and carbon dioxide, is really a compound of the bicarbonate,  $\text{NH}_4\text{HCO}_3$ , and a salt called **ammonium carbamate**,



It smells strongly of ammonia and is used to a small extent in making smelling salts, and also in baking (p. 415).



## CHAPTER XXXI

### THE ALKALINE EARTH METALS

#### CALCIUM

**Limestone.**—The most abundant calcium mineral is the carbonate,  $\text{CaCO}_3$ , crystallising as *calcite* (Fig. 349), and also in another distinct crystalline form, called *aragonite* (Fig. 350).



FIG. 349.—CALCITE FROM GUANAXUATO.  
*British Museum (Natural History).*



FIG. 350.—ARAGONITE FROM CUMBERLAND.  
*British Museum (Natural History).*

Calcite, the commoner variety, besides occurring in minerals, forms the chief constituent of eggshells and bones (together with calcium phosphate), whilst aragonite occurs in oyster-shells and coral. In the massive form calcite occurs as *marble*, *limestones* of various kinds, *calc spar* (a very pure transparent variety of which is *Iceland spar*), and *chalk*. Chalk consists of the shells of minute marine organisms. Calcium and magnesium carbonates in combination form *dolomite*,  $\text{MgCO}_3, \text{CaCO}_3$ , of which (as well as limestone) whole mountain-chains are composed.

Calcium carbonate is only very sparingly soluble in pure water, but it dissolves in water containing carbon dioxide to form an unstable bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$  (p. 298). In this form it is transported in Nature and deposited again as carbonate, *e.g.*, as *stalactites* (p. 300). The vast deposits of chalk originally existed in solution as calcium bicarbonate (p. 420).

**Quicklime**—Calcium carbonate heated to dull redness begins to decompose, evolving carbon dioxide, and leaving calcium oxide, or quicklime,  $\text{CaO}$ . In a closed vessel, the decomposition

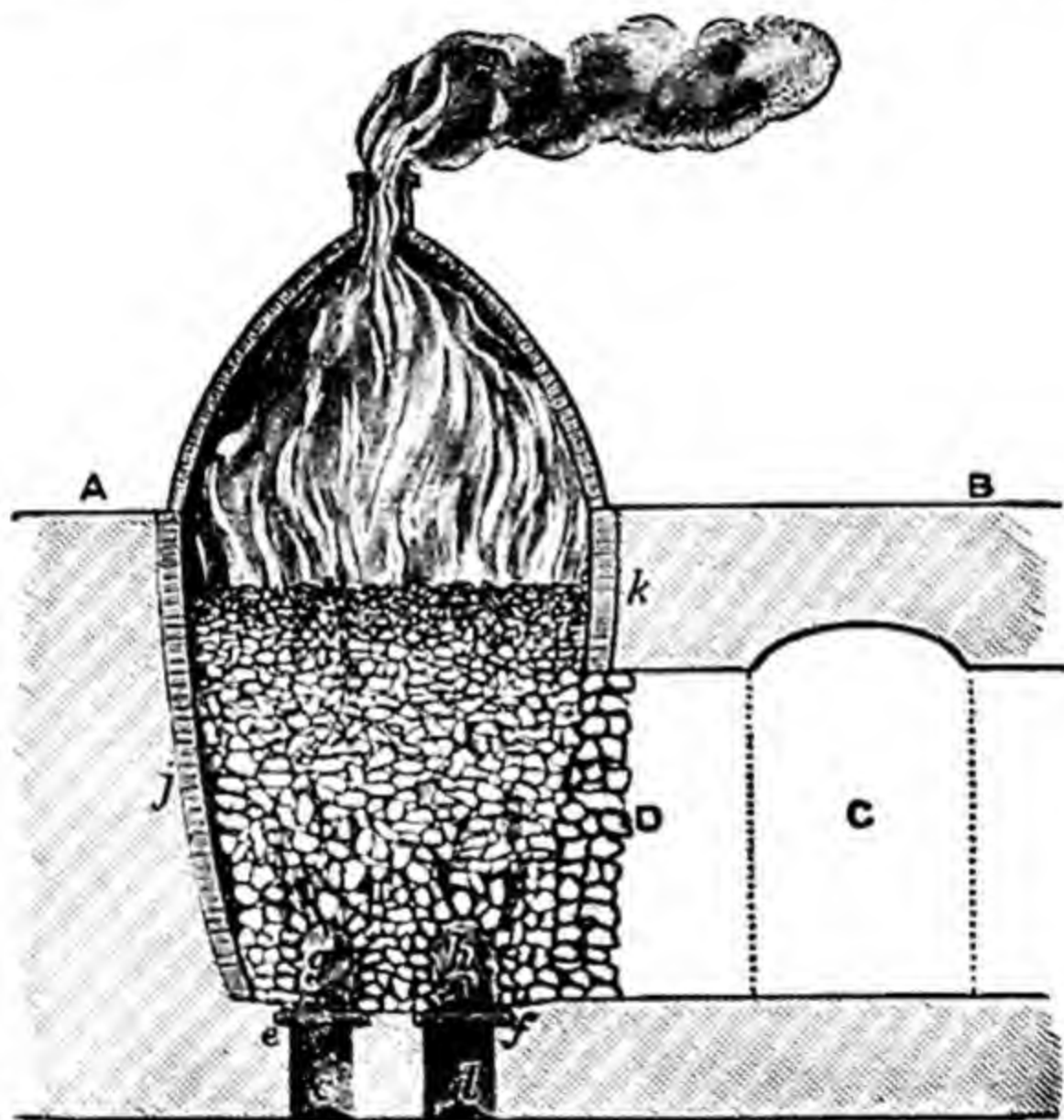
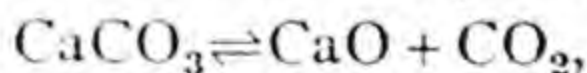


FIG. 351.—DERBYSHIRE LIMEKILN.

stops at a certain pressure of the carbon dioxide, known as the dissociation pressure, which has a definite value at each temperature; the system is then in equilibrium:



but if the carbon dioxide is swept away by a current of air, dissociation goes on till the reaction is practically complete. This is applied in the manufacture of quicklime from limestone or marble ('lime-burning') by heating to a high temperature.

In some districts, *e.g.*, in High Peak, Derbyshire, the limekiln is filled with blocks of the limestone; an arch of lumps of the stone is built over the fire below, the fuel being kept separate



from the stone (Fig. 351). The burning goes on for thirty-six to forty-eight hours, when the kiln is allowed to cool, and the lumps of quicklime (which is then nearly pure—'Buxton lime' contains 98 per cent. of  $\text{CaO}$ ) are removed. This process is somewhat wasteful in fuel, and in modern limekilns the stone passes down a tall shaft in which it is heated by burning producer gas (Fig. 352). In some types of kiln the stone is first mixed with the fuel and charged into a shaft furnace, but this gives a product mixed with fuel ash.

Pure calcium oxide is prepared by heating Iceland spar with the blowpipe in a platinum crucible, with free access of air, until a little of the white opaque residue, after cooling and addition of water, no longer effervesces with acid. It is a white, amorphous mass, which melts and volatilises only in the electric furnace. Lime resists the temperature of the oxyhydrogen blowpipe without more than sintering, and is therefore used in making furnaces for fusing platinum. These consist of two blocks of lime, hollowed out, in the lower one of which the metal is placed, whilst the blowpipe is introduced through a hole in the upper block.

**Slaked lime.**—When quicklime is moistened with water, much heat is evolved, and clouds of steam are given off. The lime combines with the water, cracks, and finally, after addition of sufficient water, crumbles down to a fine, dry, white powder. This is calcium hydroxide,  $\text{Ca(OH)}_2$ , known as *slaked lime*. If mixed with an excess of water a paste, called *milk of lime*, is formed; if shaken with water it dissolves sparingly, producing *lime water*.

Quicklime, when exposed to the air, slowly absorbs moisture and carbon dioxide, crumbling to a powder which consists of a mixture of hydroxide and carbonate. Lime water on exposure to air becomes covered with a crust of calcium carbonate.

Lime is used in the preparation of **mortar**, for building purposes, this consisting of a thick paste of slaked lime with three to four times as much sand as quicklime originally taken. Lime made from magnesian limestone slakes slowly and is called 'poor lime,' as distinguished from 'fat lime,' which slakes easily. The hardening of mortar consists in the evaporation of the moisture, or its absorption by the bricks, and the slow conversion of the hydroxide into calcium carbonate by atmospheric carbon dioxide; combination between the lime and the silica of the sand does not occur. Modern mortar usually contains ground cinders and rubbish; soluble salts from these form an efflorescence on the bricks, consisting chiefly of sodium sulphate.

Lime is also used in the manufacture of caustic soda and bleaching powder, in purifying sugar, in softening hard water, in removing hair from hides before tanning, and for whitewash. Lime is also applied to the soil. It loosens a heavy clay soil,



FIG. 352.—A MODERN LIME PLANT,

CONSISTING OF TWO PRIEST PRODUCER-GAS-FIRED VERTICAL CONTINUOUS SHAFT KILNS, THE KILNS BEING CHARGED BY MEANS OF AN INCLINED AUTOMATICALLY OPERATED DOUBLE-SKIP HOIST, WITH ELECTRIC AND HYDRO ELECTRIC CONTROL AND BELT OPERATING GEAR. EACH KILN PRODUCES OVER 200 TONS OF LIME PER WEEK ON A FUEL CONSUMPTION OF 4 CWT. OF COAL PER TON OF LIME PRODUCED.

(*Priest Furnaces Ltd.*)

neutralises the vegetable acids produced by the decay of organic matter and thus promotes nitrification, since the nitrifying bacteria cannot work in an acid soil. Spent lime from gasworks is sometimes used.



\* **Cement.**—If limestone containing clay is burnt, the resulting lime forms a mortar which hardens under water, and is therefore called **hydraulic mortar**. The later Roman mortar was sometimes of this type, and many buildings constructed with it are still standing firm. In 1796 J. Parker prepared a similar **Roman cement** by heating clay and limestone. **Portland cement** is made by burning a mixture of limestone or chalk and clay, either mixed with coal as in lime-burning, or by feeding the wet mixture into the top of a revolving tubular furnace inclined at an angle, into the lower part of which a blast of air charged with coal-dust,

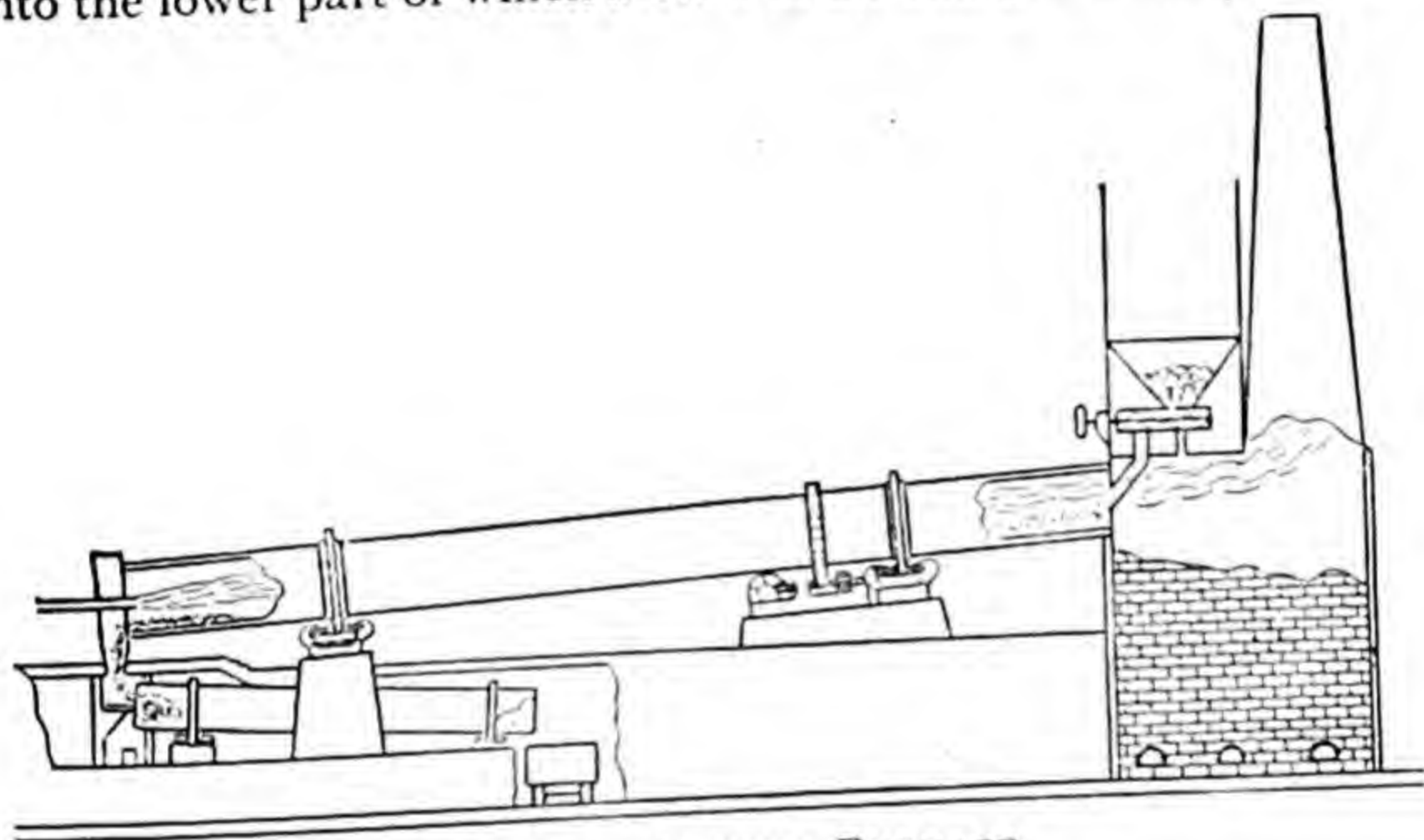
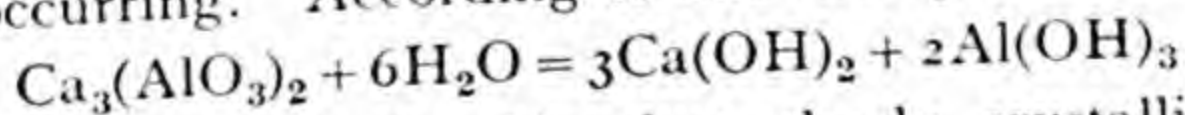


FIG. 353.—CEMENT FURNACE.

which forms an intense flame, is injected (Fig. 353). The *cement clinker* so produced is ground to powder, and packed in air-tight barrels.

The constitution of cement, and the mechanism of setting, have been variously explained. Cement clinker appears to contain silicates and aluminates of calcium, *i.e.*, compounds of  $\text{CaO}$  with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , in which the alumina ( $\text{Al}_2\text{O}_3$ ) behaves as a weakly acidic oxide. These are slowly decomposed by water, hydrolysis occurring. According to one theory the reaction :



occurs ; the calcium hydroxide then slowly crystallises and binds together the particles of calcium silicate, and the colloidal hydrated alumina ( $\text{Al}(\text{OH})_3$ ) fills up the pores of the mass. More complicated reactions probably also occur. A little

gypsum mixed with the powdered cement regulates the rate of setting. The cement sets under water.

A new kind of cement, called *bauxite cement*, *aluminous cement*, or *ciment fondu*, is made by strongly heating bauxite, a native alumina containing oxide of iron. It hardens much more rapidly than Portland cement and much time is thus saved in building or road construction.

*Concrete* is a mixture of cement and gravel; when cast over a steel frame it is called *reinforced concrete*. A cheap cement is also made by heating a mixture of powdered blast-furnace slag and limestone.

**\* Building materials.**—The common materials used for building in civilised countries are *bricks*, *stones*, *mortar*, and *cement*. Bricks, obtained from baked clay, will be considered under aluminium (*q.v.*); mortar and cement have just been described; and a few words may be said about building stones.

The stones used for building comprise essentially: (1) silica and silicates; and (2) calcium carbonate in various forms, or calcium and magnesium carbonates in association.

Silica is used in the form of sandstones, often containing 98 per cent. or more of silica, and special kinds of sandstones such as *millstone grit* and *Yorkshire flags* (for paving). Silicate rocks used in building, especially when great strength and resistance to wear and weather are required (*e.g.*, in bridges) are *granite* (p. 28), *basalt* (a fused, or *igneous* rock), and *porphyry* (a silicate of the same composition as *felspar*,  $K_2O$ ,  $Al_2O_3$ ,  $6SiO_2$ ). In modern work these stones are being replaced by the cheaper concrete.

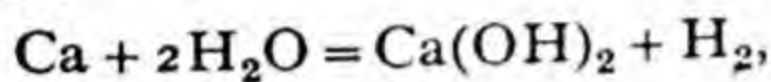
The calcium carbonate stones are more durable the more compact is their structure. *Marble*, with a very fine crystalline structure, is very resistant to weather; *Portland stone* (of which St. Paul's Cathedral is built), *Purbeck stone*, *Ancaster stone*, *Caen stone*, and *Bath stone* are good resistant varieties, but they all slowly disintegrate with the passage of time. The expansion of water in the pores of the stone by freezing hastens the process. *Dolomite*, or *magnesian limestone* ( $MgCO_3 \cdot CaCO_3$ ) is more easily cut than limestones, and is durable: the Houses of Parliament are built of it. The carbon dioxide in the air, and especially sulphuric acid from the combustion of coal, lead to corrosion of limestone. Treatment of the stone with silico-fluorides and other methods have been used in cases of corrosion: simple washing has also been urged as a remedy.

**Metallic calcium.**—Metallic calcium is prepared on a technical



scale by the electrolysis of fused calcium chloride in a bath formed of blocks of carbon, which acts as the anode. The cathode is an iron rod, on which the calcium is deposited, and this is gradually screwed up, so that a bar of metallic calcium is raised slowly from the bath (Fig. 354). It is a malleable, rather hard white metal, which burns brightly in oxygen, combines with sulphur, chlorine and nitrogen, and reduces nearly all metallic oxides on heating.

Calcium is *slowly* attacked by cold water :



and dissolves easily in dilute acids, with evolution of hydrogen.

**Calcium chloride.**—A solution of calcium chloride,  $\text{CaCl}_2$ , is obtained by dissolving calcium oxide, hydroxide, or carbonate in hydrochloric acid. When this is evaporated to a syrupy consistency, colourless deliquescent crystals of the hexahydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , separate. These crystals dissolve in water with considerable *lowering* of temperature. On heating the crystals, water is evolved, and a white, porous mass of the dihydrate,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , remains, which is used for preparing solutions for refrigerators. If heated strongly, a porous mass of the anhydrous salt is formed, which is used in drying gases, etc. This fuses at a red heat, and forms a hard crystalline mass on cooling. The dihydrate and the anhydrous salt *evolve* heat when dissolved in water. Anhydrous calcium chloride absorbs ammonia gas, forming the unstable compound,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , so that it cannot be used to dry ammonia.

Calcium chloride is formed in large quantities as a by-product in the ammonia-soda industry (p. 575). Since the solution freezes only at a very low temperature it is used in refrigeration, the strongly cooled solution being circulated through pipes, and since the salt is deliquescent it has been used for preventing the formation of dust on roads. Some calcium chloride is also used in cement manufacture.

**Calcium sulphate.**—Calcium sulphate,  $\text{CaSO}_4$ , occurs as *anhydrite* along with limestone or rock salt, or more commonly as the dihydrate *gypsum*,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which forms transparent

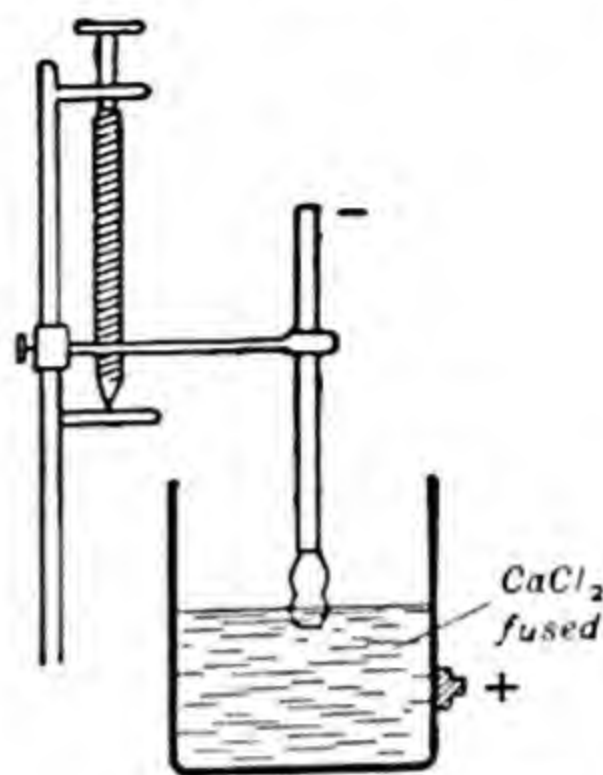


FIG. 354.—PREPARATION OF METALLIC CALCIUM.

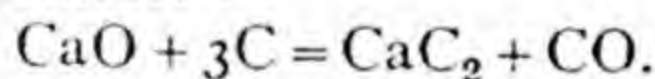
crystals called *selenite*, or occurs in crystalline masses, either fibrous (*satin spar*) or opaque (*alabaster*).

If gypsum is heated to  $120^{\circ}$ - $130^{\circ}$  it loses water and forms plaster of Paris, the hemihydrate,  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , which when mixed with water evolves heat, and quickly solidifies, expanding slightly; it is therefore used for making plaster casts in moulds. If the surface is painted with a solution of paraffin wax in petrol, the wax fills the pores, and an ivory-like surface is produced. Plaster of Paris, if heated at  $140^{\circ}$ , begins to lose water; the whole of the water is rapidly expelled at  $200^{\circ}$ ; the residue of anhydrous  $\text{CaSO}_4$  rapidly takes up water, but if the heating has been more intense the residue hydrates only very slowly, and is said to be *dead-burnt*. By heating over  $400^{\circ}$ , slight decomposition into  $\text{CaO}$  and  $\text{SO}_3$  occurs, and the German plaster called *Estrich-gips*, which sets slowly, and produces a smooth, hard surface, used for floors, walls, etc., is formed.

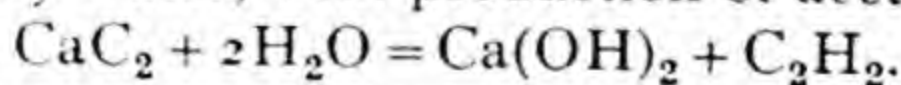
Precipitated gypsum is formed by adding sulphuric acid to a solution of calcium chloride. It is used under the name of *pearl-hardening* for 'filling' glazed paper. Barium sulphate is used for a similar purpose, giving a very heavy paper. China clay is also used as a filling. Ordinary blackboard 'chalk' is really gypsum, not calcium carbonate.

A solution of calcium hydrogen sulphite, or *calcium bisulphite*,  $\text{Ca}(\text{HSO}_3)_2$ , prepared by passing sulphur dioxide through milk of lime, is used in making paper-pulp (p. 498) and in sterilising beer casks.

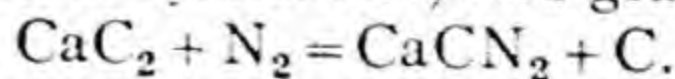
\* **Calcium carbide.**—Calcium carbide,  $\text{CaC}_2$ , is manufactured by heating a mixture of quicklime and coke in the electric furnace, at a very high temperature:



The effect (as in the production of phosphorus, p. 455) is due entirely to the high temperature and no electrolysis occurs. The product is a fused mass, which solidifies on cooling. The commercial product is a greyish-black stony mass; pure calcium carbide forms colourless transparent crystals. Calcium carbide is decomposed by water, with production of acetylene (p. 441):



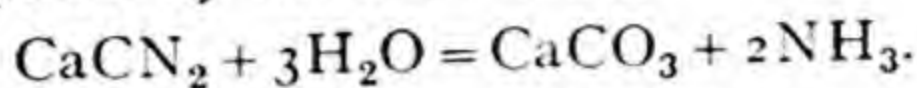
When heated in a stream of nitrogen, it reacts with the formation of a mixture of calcium cyanamide, and graphite:



The product is used as a fertiliser in agriculture. It slowly decomposes in the soil with the formation of ammonium salts,



which are valuable fertilisers, supplying the combined nitrogen required by growing plants. The powdered crude cyanamide is treated with a little water to free it from calcium carbide and then with a little oil to render it less dusty and corrosive. The cyanamide is decomposed by water as follows :

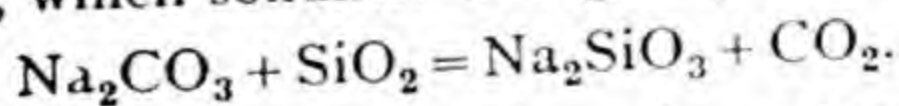


**Calcium nitrate.**—This salt,  $\text{Ca}(\text{NO}_3)_2$ , is present in the soil and serves as a plant food. It is manufactured on a large scale by neutralising dilute synthetic nitric acid with limestone, and evaporating. The fertiliser called *nitrochalk* is essentially a mixture of synthetic ammonium nitrate with precipitated calcium carbonate.

**Calcium phosphate.**—Calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is found in mineral deposits (' phosphate rock ') and in bones (' bone ash '). It is a white powder nearly insoluble in water, but on treatment with sulphuric acid it forms a mixture of an acid phosphate of calcium,  $\text{CaH}_4(\text{PO}_4)_2$ , and calcium sulphate, called *superphosphate of lime*, which is manufactured on a large scale for use as a fertiliser. Attempts have been made to replace it by ammonium phosphate, which would also supply the fixed nitrogen required by plants. Plants normally derive their phosphates from calcium phosphate in the soil, which dissolves in water containing carbonic acid and passes into the roots. When superphosphate of lime is put in the soil it is decomposed and *very finely divided* calcium phosphate is formed, which is more readily soluble. The preparation of superphosphate for agricultural purposes was invented by Sir John Lawes in 1840; he took out a patent in 1842. *Basic slag*, from the manufacture of steel (*q.v.*) is another phosphatic fertiliser containing calcium phosphate, but it often contains only very small amounts of the latter.

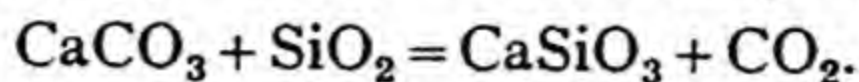
**Glass.**—The arts of making, working, and colouring glass appear to have been known to the Egyptians about 2000-1500 B.C. From Egypt the knowledge spread to Rome, Constantinople, and Venice. There were glass works in Roman Britain.

When some form of silica,  $\text{SiO}_2$ , which is an acidic oxide, is fused with sodium carbonate, the silica displaces the volatile carbonic anhydride of the latter and forms a molten mass of sodium silicate, which solidifies to a glassy mass on cooling :



The product is not suitable for use as glass, since it is soluble in water, hence its name, *water glass* (p. 472).

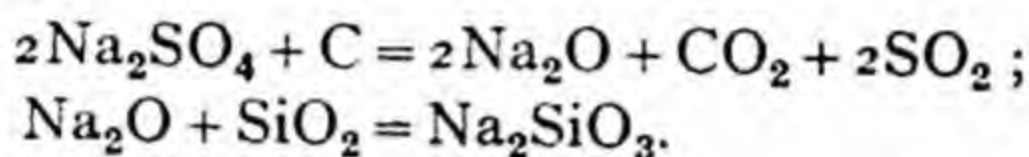
Calcium carbonate (limestone or marble) is similarly decomposed when strongly heated with silica, forming calcium silicate :



This product, which is glassy when fused, is insoluble in water but is soluble in acids.

When a *mixture* of sodium carbonate and calcium carbonate is fused with silica, the above reactions occur, but the product, which is transparent, is insoluble both in water and acids and is ordinary **glass**. A small quantity of aluminium oxide is generally present in glass.

In place of sodium carbonate, sodium sulphate is often used, generally mixed with carbon, when sulphur dioxide is evolved on heating with silica :



In making **hard glass** (potash, or Bohemian glass), which fuses at a higher temperature than common *soda glass*, potassium carbonate is used, and potassium and calcium silicates are formed. This kind of glass is used in making chemical apparatus and lenses. **Flint glass**, which has a high refractive index and is used in making lenses and prisms, is potash glass with the calcium oxide replaced by *lead oxide*, *i.e.*, it contains potassium and lead silicates. The lead is introduced by adding litharge ( $\text{PbO}$ ) or red lead ( $\text{Pb}_3\text{O}_4$ ).

The silica for glass making is generally used in the form of white sand (free from iron compounds), crushed quartz, or broken flints.

Common glass is made from 100 parts of sand, 35 to 40 of soda ash, and 15 of limestone. It has approximately the composition  $\text{Na}_2\text{O}, \text{CaO}, 5\text{SiO}_2$ . The melting temperature in the pots is about  $1375^\circ \text{C}$ . or higher. Glass is not a definite compound. It is usually regarded as a supercooled amorphous solid solution, but X-ray studies show that the metal and silicate ions make some approach to a crystalline arrangement ; the regularity is on a much smaller scale than in crystals, and may not extend more than a few atoms in distance. Even in liquids there is some tendency for the molecules to assume patterns, which are constantly broken up and re-formed.

Glass has the valuable property of becoming plastic on heating



below its melting point, and it can then be blown, moulded, or rolled into sheets (*plate glass*). Common window glass is not rolled, but is made by drawing out a cylinder of glass, cutting this along a line, and heating so that the cylinder softens and opens out into a sheet. Formerly, window glass was made by spinning with a rod a bulb formed at the end of a blowing tube, and the knob left at the place where the rod was attached was then left on the sheet and is seen on panes of glass in old windows.



FIG. 355.—BLOWING GLASS.

This is, of course, imitated in modern 'antique' glass, just as wormholes are produced artificially in modern 'antique' furniture. Wonderful machines for drawing the huge cylinders of glass used in making sheets, and for blowing bottles, have been invented.

The Owen's bottle-making machine is arranged so that six vertical portions, by rotation of the machine, come in turn over the tank of molten glass, when a mould is dipped into the glass. Suction is then automatically applied and glass drawn into the upper mould. This is raised from the tank, the glass cut off below by a knife, and the lower mould is closed round the glass, the upper mould opening out and the lower one coming up from below. Compressed air is then turned on and the bottle blown out in the mould. The mould then opens, the bottle is taken out, and

the upper mould again comes over the tank of glass for the operations to begin again (Figs. 356-57).

**Jena resistance glass** has a low alkali content, a higher alumina content (which confers toughness) than ordinary glass and contains boron trioxide (p. 474) in place of some silica.

A glass very rich in silica, poor in alkali and alumina, and containing boron trioxide,  $B_2O_3$ , is called *Pyrex* (p. 21): it is

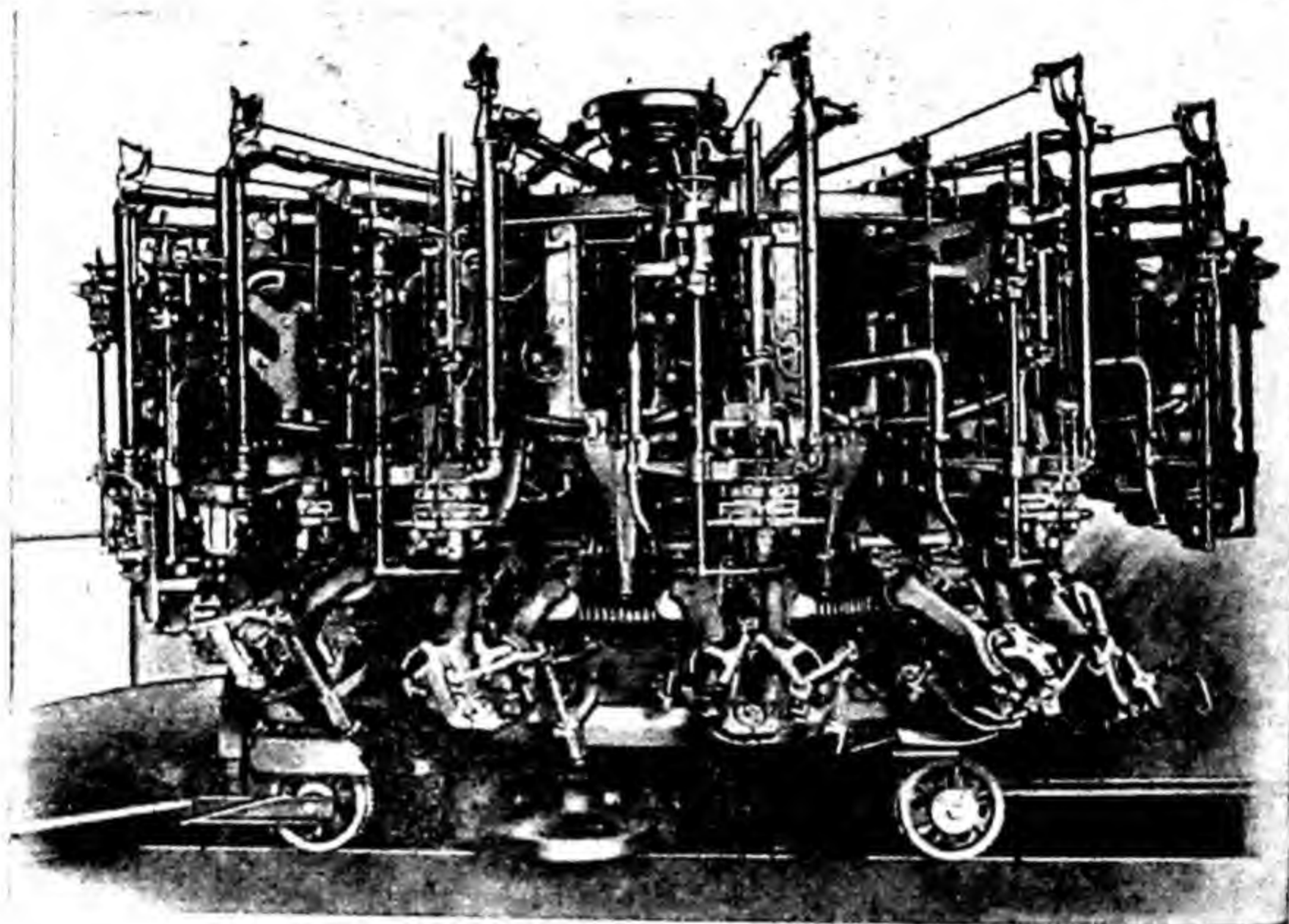


FIG. 356. — OWEN'S BOTTLE MACHINE.

very resistant to heat and to sudden changes of temperature, and is made in high temperature tank furnaces. A similar glass is *Monax*.

Optical glasses, for lenses, often contain special constituents, such as boron trioxide and phosphorus pentoxide, in place of silica, barium oxide in place of lime, and sometimes zinc oxide. Two main divisions of optical glasses are recognised: **crown glass**, containing as basic oxide mainly potash or barium oxide; and **flint glass**, containing lead oxide. By combining lenses of these two types, dispersion is eliminated (Hadley, *Everyday Physics*, p. 205). *Crookes's glass*, for spectacles, contains rare earth compounds (praseodymium and neodymium): it allows visible light to pass but absorbs the ultra-violet. A glass containing



nickel, on the contrary, which is very dark red, absorbs nearly all the visible light but allows a part of the ultra-violet spectrum to pass through. Ordinary glass absorbs the infra-red rays (radiant heat), hence its use for glass firescreens.

If good glass is heated to its softening point for a long time or inferior glass for a short time, some of the constituents crystallise,

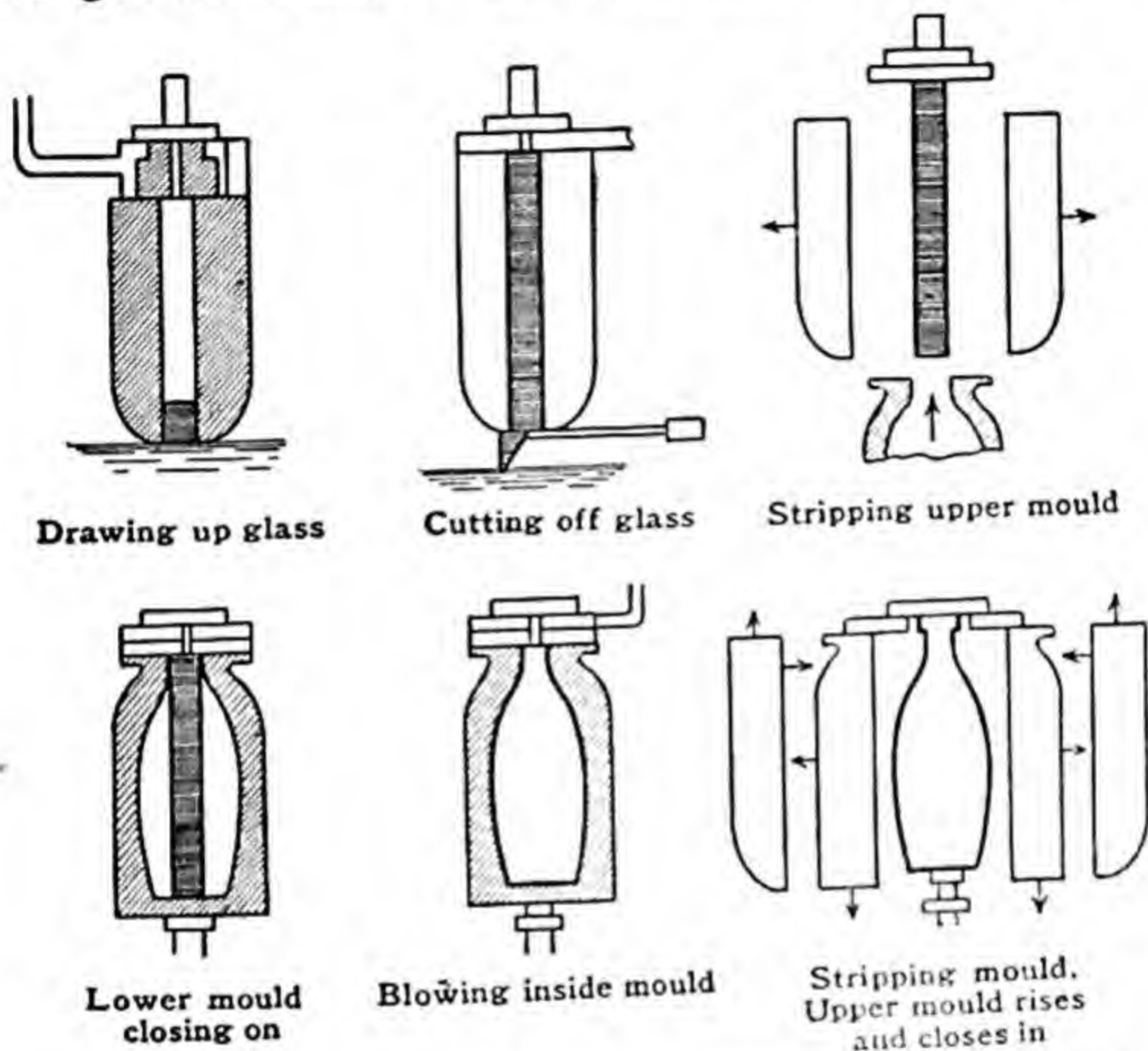


FIG. 357.—BLOWING BOTTLES IN THE OWEN'S MACHINE.

and the glass becomes opaque (*devitrification*). All varieties of glass require *annealing* before use: the objects are heated for a time and allowed to cool slowly. Toughened glass is obtained by cooling in oil.

**Coloured glasses** are made by adding various metallic oxides or other substances. The following are the main varieties:

**Ruby**: gold; selenium; cuprous oxide.

**Green**: chromic oxide; cupric oxide with chromic or ferric oxides and an oxidising agent.

**Yellow**: carbon and sulphates in the melt; cadmium sulphide; sometimes uranium or selenium.

**Violet** : manganese dioxide. **Blue** : cobalt oxide.

**Opaque milky glass** : fluorspar with felspar ; cryolite ; sometimes tin oxide or calcium phosphate.

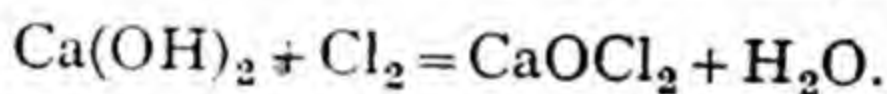
**Fluorescent greenish-yellow** : uranium oxide.

**Black** : large quantities of ferric oxide and cupric oxide or cobalt, nickel, and manganese oxides.

**Artificial gems** are frequently coloured glasses, although real but artificial rubies and emeralds are made by fusing aluminium oxide with small quantities of metallic oxides.

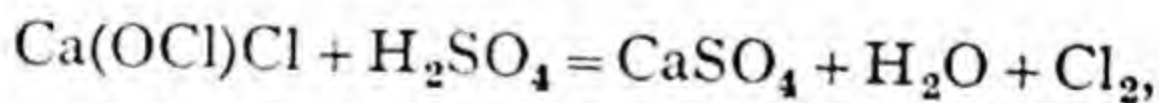
Since the materials used in making common glass contain iron compounds, these are reduced to ferrous oxide,  $\text{FeO}$ , which colours the glass green. This can be removed by adding arsenic oxide, potassium nitrate or manganese dioxide (*pyrolusite*—a material which ‘cleanses by fire’) when  $\text{Fe}_2\text{O}_3$  is formed, which has practically no colour in small amounts. Glasses made from materials containing only very little iron or titanium are more permeable to ultra-violet light than ordinary glass.

**Bleaching powder**.—By the action of chlorine gas on dry slaked lime bleaching powder (also called *chloride of lime*—not to be confused with calcium chloride) is formed. This was formerly thought to have the formula  $\text{CaOCl}_2$  or  $\text{Ca}(\text{OCl})\text{Cl}$  :



More recently it has been regarded as a mixture of calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ —now made commercially as *maxochlor*—and a non-deliquescent basic calcium chloride,  $\text{CaCl}_2, \text{Ca}(\text{OH})_2, \text{H}_2\text{O}$ .

Bleaching powder is an oxidising agent and is used in bleaching (p. 325) and as a disinfectant. It becomes moist on exposure to air and does not keep in a hot climate. Strong acids liberate *all* the chlorine of bleaching powder :



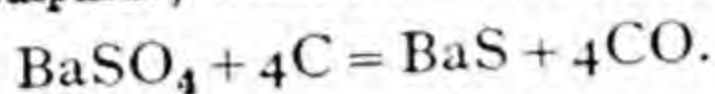
so that the whole of the chlorine (not simply the hypochlorite chlorine) is *available chlorine*.

**\*Strontium and barium**.—Strontium occurs as minerals in the form of the sulphate,  $\text{SrSO}_4$ , and carbonate,  $\text{SrCO}_3$ . The hydroxide,  $\text{Sr}(\text{OH})_2$ , is sometimes used in refining sugar, and the nitrate,  $\text{Sr}(\text{NO}_3)_2$ , in making *crimson fire*, a mixture of the nitrate or chlorate,  $\text{Sr}(\text{ClO}_3)_2$ , charcoal, and sulphur, which burns with an intense red flame. Barium is found as sulphate,  $\text{BaSO}_4$ , in the dense mineral *heavy spar*, and as the carbonate,  $\text{BaCO}_3$ , as *witherrite*.



Precipitated barium sulphate is used as a white pigment; a mixture of it with precipitated titanium oxide ( $\text{TiO}_2$ ) is known as *barium white*. Barium is found as **sulphate**,  $\text{BaSO}_4$ , in the dense mineral *heavy spar*, and as the **carbonate**,  $\text{BaCO}_3$ , as *witherrite*.

Precipitated barium sulphate is used as a white pigment; a mixture of it with precipitated titanium oxide ( $\text{TiO}_2$ ) is known as *titanium white*. When heated with carbon the sulphate is reduced to barium sulphide, used in making *lithopone* (q.v.):



The **chlorate** and **nitrate** are used in pyrotechny in making *green fire*. Barium carbonate is scarcely decomposed at a red heat: the **oxide** (baryta) is best obtained by heating the nitrate. It absorbs oxygen at a dull red heat, forming the **peroxide**,  $\text{BaO}_2$ . Soluble barium compounds are poisonous. Barium **chromate**,  $\text{BaCrO}_4$ , is a yellow pigment added to lead chromate and also used as an oxidising agent in the match industry.

\* **Radium**.—A very remarkable member of the group of alkaline-earth metals is radium. Radium compounds are used in surgery and in making self-luminous dials for watches. The **bromide** is generally used.

Radium is itself a product of the disintegration of **uranium**, being preceded by another radioactive element called **ionium**, discovered by Boltwood. Uranium compounds quite free from radium 'grow' this element on keeping, so that uranium is the 'grandparent' of radium, the immediate parent being ionium.

Radium is obtained from pitchblende from the Belgian Congo, Czecho-Slovakia, Portugal, and the Great Bear Lake territory in North-West Canada (which produces the richest ore known). The annual production is only a few grams and the average price before 1939 was about 50 dollars per milligram of radium in the form of bromide.

## CHAPTER XXXII

### MAGNESIUM AND ZINC

**Magnesium.**—In 1695, Nehemiah Grew obtained from the water of a mineral spring at Epsom a peculiar salt which was called **Epsom salts**; it is **magnesium sulphate**,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; **magnesium chloride**,  $\text{MgCl}_2$ , is contained in sea water and in the mineral *carnallite* found at Stassfurt (p. 579). By precipitating solutions of these salts with sodium carbonate, *magnesia alba*, which like Epsom salt is used medicinally, is obtained. Black, in 1754, showed that *magnesia alba* is a compound of fixed air, or carbon dioxide, with *calcined magnesia*, or **magnesium oxide**,  $\text{MgO}$ , left after ignition of *magnesia alba*. Metallic magnesium was obtained in an impure state by Davy.

Magnesium is widely distributed, occurring in the forms of *magnesite*,  $\text{MgCO}_3$ ; *dolomite*,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ ; and *carnallite*,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . *Talc* ('French chalk'), *asbestos*, and *meerschauum* all contain magnesium silicates. All plant and animal tissues contain magnesium; it is an essential constituent of *chlorophyll*, the green colouring matter of plants (p. 420).

Commercial asbestos consists of the fibrous varieties of several minerals (amphiboles, such as actinolite, anthophyllite; horn-blendes, such as tremolite, true asbestos, mountain leather, crocidolite, etc.; and serpentines, such as picrolite, chrysotile and fibrous talc). The value of the material depends on its occurrence in long fibres capable of being spun. *Blue asbestos* contains a larger quantity of iron and is very resistant to acids.

Metallic magnesium prepared by the electrolysis of fused carnallite, and pressed into ribbon, burns when heated in air with an intense white light, producing the oxide,  $\text{MgO}$ , and a little nitride,  $\text{Mg}_3\text{N}_2$ . The residue, when moistened with water, therefore gives off a little ammonia. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively when lighted, producing a blinding white flash, used in photography, and for signalling and star-shells. The metal



is stable in dry air, but soon becomes covered with oxide in moist air. It is very light (sp. gr. 1.75). Fine crystals are formed by subliming the metal in an evacuated tube. The metal dissolves readily in dilute acids, but not in alkalies. Magnesium powder decomposes water. The metal is a constituent of some light alloys (p. 567).

**Magnesium oxide**,  $\text{MgO}$ , is usually prepared by heating the basic carbonate (*q.v.*), or native magnesite, and is known as *calcined magnesia*. The oxide slowly combines with water, forming the hydroxide,  $\text{Mg}(\text{OH})_2$ , and when moist turns red litmus paper blue.

Magnesia, prepared by the calcination of native magnesite, is used in the manufacture of *refractory bricks* for electric furnace linings. These are *basic*, and resist the action of basic slags containing lime. *Acidic* linings are composed of ganister (largely silica), and *neutral* linings of chromite or chrome iron-stone (*q.v.*). A mixture of magnesia and asbestos is used as a 'lagging' for pipes to retard the transmission of heat. It does this on account of the air enclosed in its pores, which is a bad conductor of heat. **Magnesium peroxide** is contained in some kinds of tooth-paste: it liberates hydrogen peroxide with water.

The **normal carbonate**,  $\text{MgCO}_3$ , occurs native as *magnesite*. The precipitates formed by adding carbonates to solutions of magnesium salts are always **basic carbonates**. From solutions at the ordinary temperature, the precipitate is a light loose powder—*magnesia alba levis*—of variable composition. From a boiling saturated solution, a denser crystalline precipitate is thrown down, this is evaporated to dryness, washed, and dried at  $100^\circ$ , and is known as *magnesia alba ponderosa*. Both are used in medicine. If the basic salts are suspended in water, and a current of carbon dioxide is passed through, they dissolve, producing a *bicarbonate*. The solution is known as *fluid magnesia*.

**Magnesium chloride**,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , obtained from carnallite (p. 579), when mixed in solution with solid magnesium oxide, sets to a hard solid called *Sorel's cement*, used for flooring plaster.

\***Beryllium**, a metal closely related to magnesium, which is ductile at high temperatures like tungsten, has a lower specific gravity (1.84) than aluminium (2.7) and finds application in the manufacture of alloys. It is found as the mineral *beryl*, a silicate of aluminium and beryllium. Beryllium salts are used in making incandescent gas mantles (p. 431).

## ZINC.

**Zinc.**—The metal *orichalcum*, mentioned by Plato (400 B.C.) as forgotten in his day, may have been brass, an alloy of zinc and copper. Similar alloys were used long before this in China, and true brass of the period 1500 B.C. was found at Gezer in Palestine. The material called *cadmia*, from which brass was obtained in the Roman period by reduction with charcoal in presence of copper, was zinc carbonate, and zinc oxide is described by Dioskorides (p. 62).

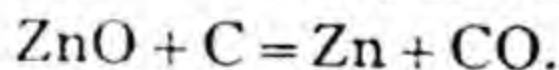
Although brass, the alloy of zinc and copper, was known in early times, the metal zinc itself is first described by Strabo (60-20 B.C.) as 'false silver,' and he also describes its preparation. An idol from Thrace, of about the time of Strabo, has been found on analysis to consist of impure zinc. The use of the metal appears to have been forgotten in Europe until about 1500 A.D. when it is again mentioned by Paracelsus and by Agricola. It was made in the East Indies and imported as 'Indian tin': its production in Europe began about 1700 by a method based on information obtained from the East Indies. At present zinc is largely prepared in Belgium, Germany, and America.

**Preparation of zinc.**—The principal zinc ores are *zinc blende* (zinc sulphide,  $\text{ZnS}$ ), *calamine* (zinc carbonate,  $\text{ZnCO}_3$ ), and ores containing zinc oxide. The ores are roasted, when zinc oxide is



FIG. 358.—TECHNICAL PREPARATION OF ZINC.

formed, and this is then strongly heated in fireclay retorts with carbon, when zinc, which is volatile, distils over (Fig. 358):



The metal condenses partly as a powder mixed with oxide, as *zinc dust*, and partly as fused metal. For use in the laboratory the zinc (sometimes called *spelter*) is melted in a fireclay crucible and poured into water, when *granulated zinc* is obtained.

The metal is not easily attacked by air, and iron sheets are *galvanised* by cleaning them and dipping them into melted zinc, when a thin sheet of zinc adheres to the iron.



Zinc is also used in making brass, and for the negative poles in galvanic cells (p. 214).

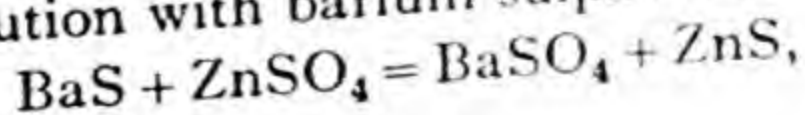
**Cadmium**, a metal which occurs in zinc ores and is produced in the metallurgy of zinc, has recently been applied in *cadmium plating*. An amalgam of cadmium is used in stopping teeth, and the sulphide,  $\text{CdS}$ , is used as a yellow pigment.

**Compounds of zinc.**—Zinc burns brightly when strongly heated in air, forming **zinc oxide**,  $\text{ZnO}$  (*cf.* magnesium). This is also obtained by heating the **hydroxide**,  $\text{Zn(OH)}_2$ , or **carbonate**,  $\text{ZnCO}_3$ , which are white precipitates thrown down from solutions of zinc salts (*e.g.*, zinc sulphate) by adding caustic soda, or sodium carbonate, solutions, respectively. (The carbonate formed is a *basic salt*.) Zinc oxide is a white powder which becomes yellow on heating, recovering its whiteness on cooling. It is used as a white pigment (*Chinese white*), in medicine for dusting on the skin or as zinc ointment, but its most important uses are as a filler for rubber (55 per cent. of zinc oxide) and in making linoleum (p. 518).

**Zinc chloride**,  $\text{ZnCl}_2$ , is obtained in the anhydrous form by heating zinc in chlorine or hydrogen chloride gas. The crystalline substance is obtained by dissolving zinc, or its oxide or carbonate, in excess of hydrochloric acid and evaporating. The solid obtained is usually fused and cast into sticks, used as a caustic. On heating strongly it loses hydrochloric acid and forms an oxychloride,  $\text{Zn}_2\text{OCl}_2$ , which is also formed from the oxide and a syrupy solution of zinc chloride: the mass sets very hard and is used as a dental stopping. Zinc chloride is an antiseptic and is used in impregnating timber to prevent *dry-rot*. Fluorides are used for the same purpose.

Zinc chloride solution slowly 'digests' cellulose to a plastic mass which may be moulded, the zinc chloride washed out, and the mass dried. In this way fibre boards, fibre buckets, etc., are formed.

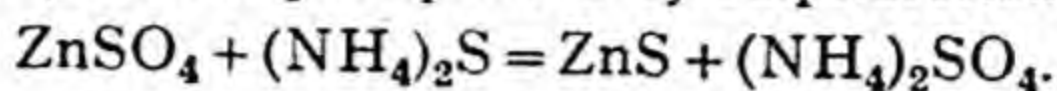
**Zinc sulphate** forms crystals,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , isomorphous with Epsom salts, and called *white vitriol*. Other vitriols (*i.e.*, glassy salts) are *blue vitriol* ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and *green vitriol* ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). Zinc sulphate is easily obtained by dissolving the metal, oxide, or carbonate in dilute sulphuric acid and evaporating till the liquid crystallises on cooling. It is used in dilute solution as an eye-lotion, and in the manufacture of *lithopone*, which is a white pigment obtained by precipitating zinc sulphate solution with barium sulphide:





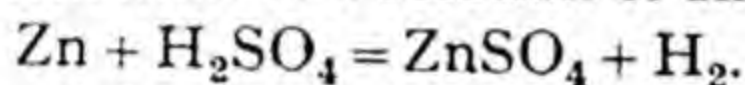
and heating. Both barium sulphate and zinc sulphide are insoluble. Lithopone is not, like white lead, turned black by sulphuretted hydrogen. It darkens on exposure to light but becomes white again in the dark.

Zinc sulphide,  $\text{ZnS}$ , is formed as a white precipitate when ammonium sulphide is added to a solution of zinc chloride or zinc sulphate (it is *not* precipitated by sulphuretted hydrogen) :

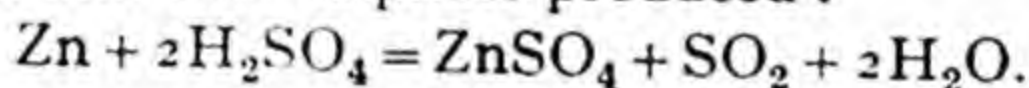


It dissolves readily in dilute acids, with evolution of sulphuretted hydrogen. Zinc sulphide exhibits the property of phosphorescence, shining in the dark after exposure to light. The phosphorescence is only temporary, but is renewed by re-illumination. It also phosphoresces when exposed to X-rays, and is used in making screens for X-ray work, and also when exposed to rays from radium. The perfectly pure sulphide is said not to exhibit phosphorescence. Calcium sulphide is also a phosphorescent substance.

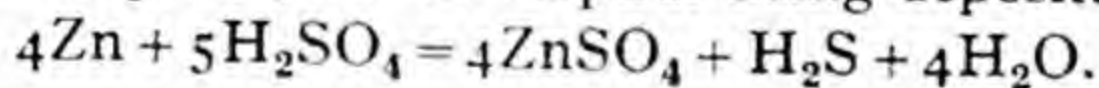
Dilute sulphuric acid dissolves zinc in the cold, with evolution of hydrogen and formation of a solution of zinc sulphate :



Hot concentrated sulphuric acid dissolves zinc, sulphur dioxide being evolved and zinc sulphate produced :



A mixture of 2 vols. of concentrated sulphuric acid with 1 vol. of water evolves hydrogen sulphide when heated with zinc, forming zinc sulphate, a little sulphur being deposited :



**\*Mercury.**—The liquid metal mercury belongs to the same group as magnesium, zinc, and cadmium. It occurs as the sulphide,  $\text{HgS}$ , a bright red substance called *cinnabar* or *vermilion*, from which it is obtained by heating in air :  $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$ . It oxidises slowly when heated in air, forming red mercuric oxide,  $\text{HgO}$ . Vermilion is also made from mercury and sulphur for use as a pigment.

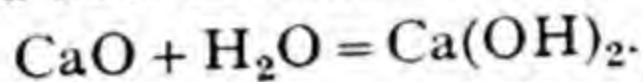
Unlike zinc, mercury forms two series of compounds, the mercurous, such as mercurous chloride,  $\text{HgCl}$  (or  $\text{Hg}_2\text{Cl}_2$ ), the medicine *calomel*; and the mercuric, such as mercuric oxide and the intensely poisonous mercuric chloride,  $\text{HgCl}_2$ , known as *corrosive sublimate* and used in very dilute solution as an antiseptic. Mercury fulminate,  $\text{Hg}(\text{CNO})_2$ , is used as a *detonator* (p. 527).



Mercury is used in making thermometers and barometers : it was formerly used with tinfoil in making mirrors, but these are now silvered (*q.v.*). Its common name *quicksilver* means 'living silver' (*cf.* 'the quick and the dead' in the Bible) and is derived from the Latin name *argentum vivum*. The metal is distinctly volatile at room temperature, giving off a poisonous vapour which can be photographed by means of ultra-violet light as it rises from the metal.

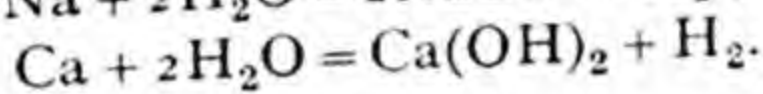
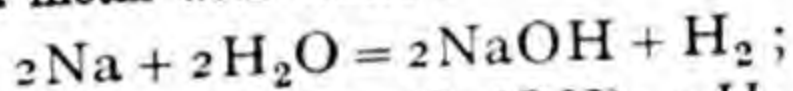
**The formation of bases.**—We may recapitulate the reactions leading to the formation of bases, *i.e.*, compounds of an electro-positive metal or radical with hydroxyl,  $-OH$ . These are :

- (1) Direct union of a basic oxide with water :

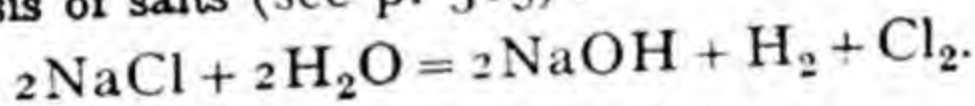


Certain *peroxides* with water give the base (corresponding with the lower oxide) and oxygen gas, *e.g.*, sodium peroxide (p. 281).

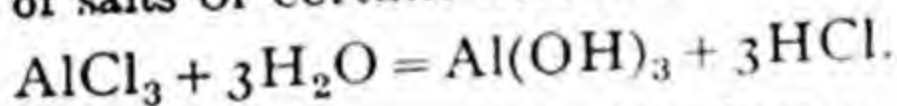
- (2) Reaction of a metal with water :



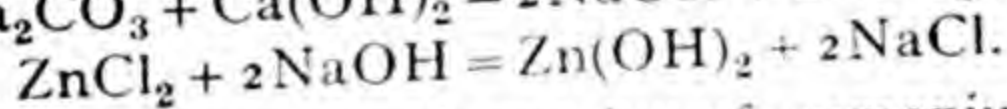
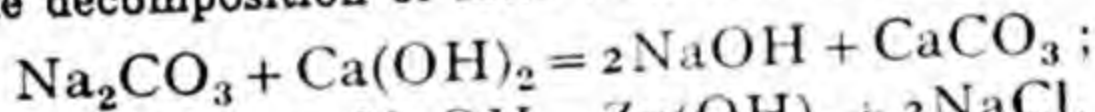
- (3) Electrolysis of salts (see p. 315) :



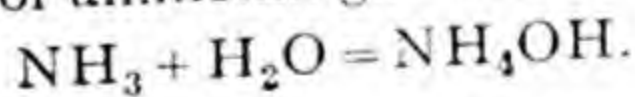
- (4) Hydrolysis of salts of certain metals :



- (5) Double decomposition of salts with other bases:



- (6) A special method is the formation of ammonium hydroxide by the combination of ammonia gas with water :



## CHAPTER XXXIII

### ALUMINIUM

**Aluminium.**—The familiar white metal aluminium always occurs in combination with oxygen as the oxide *alumina*,  $\text{Al}_2\text{O}_3$ , in the forms of *corundum* and *emery*, and combined with other oxides in rocks and in clay. Clay is essentially an impure hydrated aluminium silicate,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , derived from the disintegration of rocks, the purest form being *China clay* or *kaolin*. Clay always contains some free silica. *Fuller's earth* is a non-

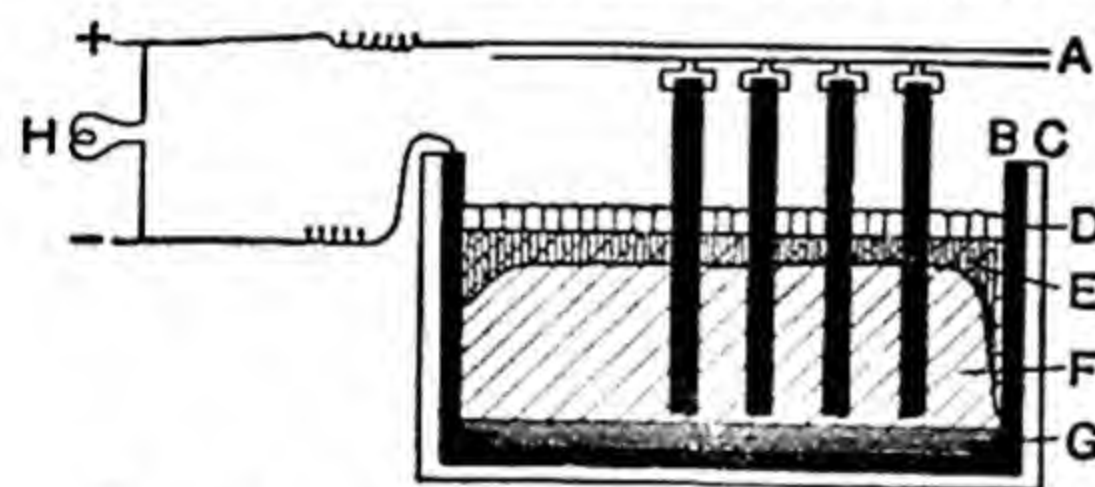


FIG. 359.—TECHNICAL PREPARATION OF ALUMINIUM.

A, LEAD TO CARBON ANODES; B, CARBON LINING; C, OUTER IRON VESSEL; D, CARBON POWDER PROTECTING SURFACE OF ELECTROLYTE; E, CRUST OF SOLIDIFIED ELECTROLYTE; F, MOLTEN ELECTROLYTE; G, MOLTEN METAL; H, CONTROL LAMP.

plastic clay used for decolorising oils, etc. (cf. p. 409). The metal was obtained by Wöhler in 1827 by the action of potassium on the chloride,  $\text{AlCl}_3$ . It is not possible to prepare aluminium, which is a very useful metal, directly from clay, but it is obtained from *bauxite*, a mineral which is an impure hydrated oxide of aluminium, by first purifying it, and then electrolysing the oxide dissolved in fused *cryolite*, or mineral double fluoride of aluminium and sodium,  $\text{Na}_3\text{AlF}_6$ , found in Greenland. The electrodes are of carbon, and the oxygen liberated combines with the electrodes to form carbon monoxide. This is a process of true electrolysis.

Large works are operated by the British Aluminium Company in Scotland and in North Wales, using water power for generating the electric current, and large quantities of aluminium are also produced in America and on the Continent.



The process for making aluminium was invented by an American student, Charles Martin Hall, at the age of 22. Hérault, in France, invented an almost identical process a few months later, quite independently. Castner, just before this, had worked out a different process, making use of sodium, but this had to be given up, so Castner went on to the invention of the alkali cell (p. 315). This cell was not regarded favourably by technical experts, but Sir Henry Roscoe, who was professor of chemistry in Manchester, strongly advocated Castner's claims and, in the form of the Castner-Kellner cell, the process proved a great success. The price of aluminium fell in 1890-1900 from 25s. to 2s. per kg. In 1932 it was 1s. 6d.

Aluminium is fairly resistant, its surface being covered by a thin transparent 'varnish' of oxide which prevents further attack. It is a very light and fairly strong metal, readily worked, but melts rather easily ( $659^{\circ}$ ). An alloy of aluminium with 2 to 10 per cent. of magnesium, sometimes with a small amount of manganese, is lighter than aluminium and is used for pistons of motor engines and for a variety of other purposes for which a light alloy is suitable. *Duralumin* is an alloy of aluminium with small amounts of copper, manganese and magnesium: it can be tempered like steel and is very strong. Aluminium wires are used to some extent for carrying electric currents, and the metal for cooking utensils, and for de-oxidising molten steel.

**Aluminium powder** is produced by stamping small pieces of thin sheet in the presence of a small quantity of grease. It really consists of very thin flakes which, when made into paint, rise to the surface of the medium and aggregate to a film, so that less material is required to produce an opaque surface than with ordinary pigments, the particles of which are granular. Aluminium paint is used for protecting oil storage tanks from the heating effects of the sun and for reducing corrosion of iron.

*Aluminium bronzes* contain copper alloyed with aluminium to the extent of 3 to 10 per cent. They are homogeneous, hard, and of high tensile strength, and are practically not corroded by sea water, especially if manganese is also present.

**Thermit.**—A mixture of ferric oxide and aluminium powder is called thermit: when ignited by a special fuse it burns with remarkable vigour, and a mass of molten iron is formed:  $\text{Fe}_2\text{O}_3 + 2\text{Al} = 2\text{Fe} + \text{Al}_2\text{O}_3$ . The temperature rises so high that the alumina is also fused, although the melting point of this



oxide is over  $2000^{\circ}\text{C}$ . The molten iron may be tapped from the crucible directly on the junction of two steel rails which are to be welded together, or the metal may be run on to such objects as broken parts of machinery in order to repair them. Thermit

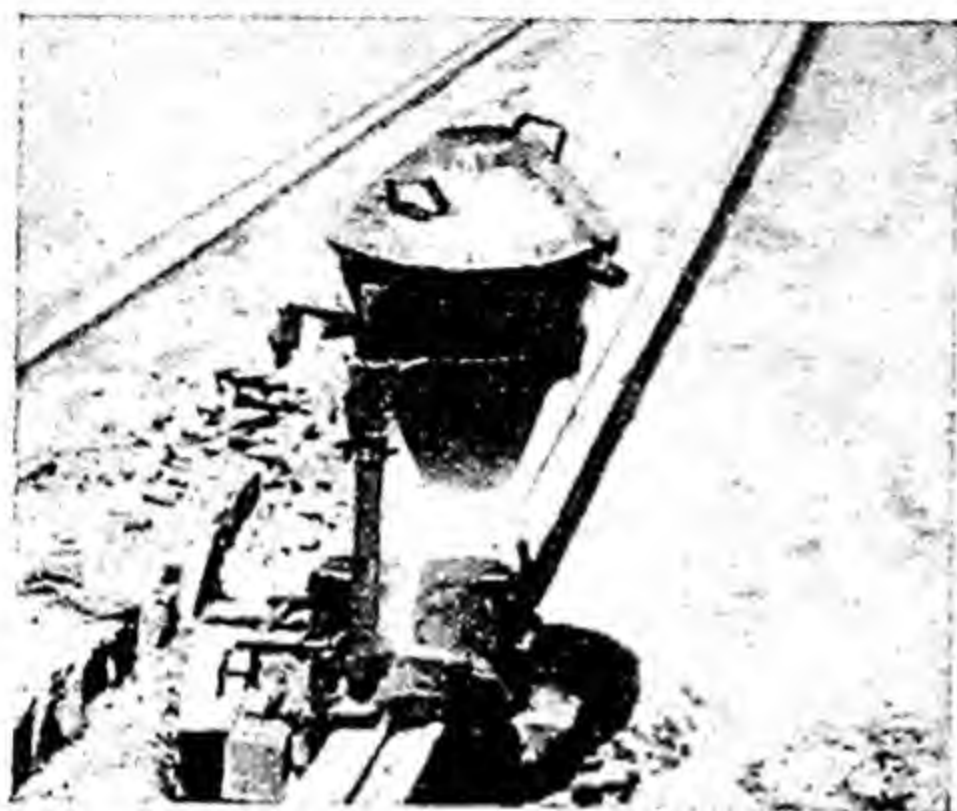


FIG. 360.—USE OF THERMIT.

has been replaced to some extent by electric welding in cases where a mere joining of two pieces of iron or steel, as contrasted with building up missing metal, is required.

**Alumina.** — Aluminium oxide, or alumina,  $\text{Al}_2\text{O}_3$ , occurs as *emery*: an artificial form called *alundum* is obtained by fusing the oxide in the electric furnace and is used, like emery, as an abrasive and also as a refractory. Hydrated alu-

minium oxide, sometimes regarded as **aluminium hydroxide**,  $\text{Al}(\text{OH})_3$ , is precipitated as a gel (p. 179) when an alkali is added to a solution of an aluminium salt. It is soluble in excess of caustic potash or soda, but is not soluble in ammonia. It is a basic oxide, but also shows feebly acidic properties, forming salts called **aluminates** with *strong* alkalies.

Precipitated alumina gel tends to adsorb substances from solution, *e.g.*, proteins. The adsorptive properties of alumina have been used in purifying sewage: aluminium sulphate and lime are added and the precipitated gelatinous alumina carries down both fine suspended matter and also dissolved organic matter. It is also utilised in making the pigments called **lakes**: the colour in solution is mixed with alum and the hydrated aluminium oxide thrown down with an alkali. It carries with it the colour, and the powder when dry is called a lake. *Carmin lake* (*crimson lake*) is prepared in this way from a water solution of *cochineal*, the dried insect *Coccus cacti* which is found on a species of cactus in Mexico and Peru. Lakes are generally expensive pigments and the colours are not always very permanent (p. 531).

**Aluminium sulphate.**—This salt,  $\text{Al}_2(\text{SO}_4)_3$ , finds a number of uses, *e.g.*, in conjunction with rosin soap it is used in sizing paper (p. 498). It is made by treating calcined kaolin with hot



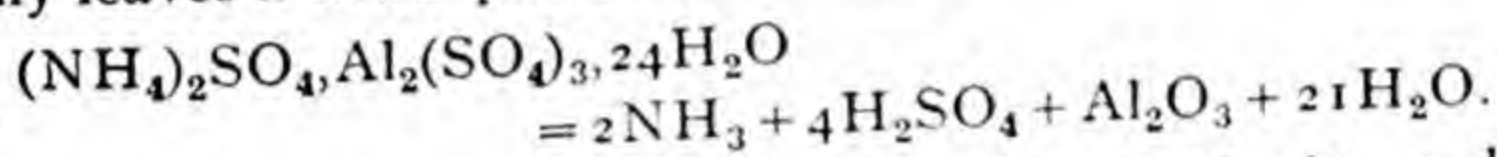
sulphuric acid, when reaction occurs and a solid called *alum cake* is formed, containing the silica and impurities of the clay. This is lixiviated with water and the aluminium sulphate crystallised as 'white sulphate of alumina.' Bauxite is also used instead of kaolin. Aluminium sulphate is now largely replacing alum in technical processes, although alum crystallises better and is more easily purified.

Common alum is a double salt of aluminium sulphate with either potassium sulphate or ammonium sulphate, and water of crystallisation :

potassium alum :  $K_2SO_4, Al_2(SO_4)_3, 24H_2O$  ;

ammonium alum :  $(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$ .

Both form white, transparent, octahedral crystals and are isomorphous (p. 187). Potassium alum on heating loses water of crystallisation and leaves a white amorphous residue of  $K_2SO_4, Al_2(SO_4)_3$ , called *burnt alum*. Ammonium alum on heating melts, loses water, ammonia and sulphuric acid and finally leaves a white powder of alumina :



Alum is manufactured from the mineral *alunite*, a basic aluminium potassium sulphate, and from *alum shale*. The alum shale is roasted, by which aluminium sulphate is formed, and this is lixiviated out and crystallised after addition of potassium or ammonium sulphate. Alum is used as a mordant, in tanning (p. 536), and in medicine as an astringent. It is described by Pliny.

**Pottery and porcelain.**—The basis of bricks, pottery, and porcelain is clay in varying degrees of purity. This clay is fine grained, semi-colloidal, easily moulded when moist and retaining its shape on drying and on heating, although some contraction occurs. Bricks, both sun-dried and baked, were used in ancient Egypt and Babylonia. Pottery was also made in very early periods in both these lands. The clay used for bricks is impure, containing oxide of iron which gives them a red colour.

The manufacture of true *porcelain*, a pure white, translucent, non-porous ceramic, as hard as steel, appears to have been discovered in China in the seventh or ninth century A.D. It did not reach Europe until 1498. The method of manufacture was discovered in 1709 by Tschirnhaus, or his assistant Böttiger, at Meissen in Saxony, where a factory was started in 1710, although

white porcelain was first exhibited in 1713. The earlier work of Bernard Palissy (1509-1589) was directed mainly to the glazing and colouring of pottery, or earthenware, as distinct from porcelain.

Clay for making pottery or porcelain is washed to separate coarser particles, which settle out, and is then allowed to stand. In England it is mixed with finely-ground calcined flints and felspar or Cornish stone, a partly weathered felspar. The plastic mass is formed on the potter's wheel (Fig. 361), dried in warm rooms, and then fired in kilns (Fig. 362).



FIG. 361.—FORMING POTS FROM CLAY ON THE WHEEL.

The **pottery furnace** consists of a cylindrical tower with a perforated domed top, built of refractory bricks, with the eight or ten fireplaces arranged on the outside, and communicating by ports with the inside where the goods are stacked inside fireclay boxes called *seggars*. The whole is covered with a bottle-shaped housing of brick, called a *hovel*, which is all that is seen from the outside (Fig. 362). The hot gas and smoke from the furnace pass out from the top of the hovel.

In the process of firing clay, the particles at the highest temperature undergo partial fusion and become cemented together, forming a stony mass. Clay which contains a large proportion of silica and alumina in comparison with the basic oxides ( $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ) always present as impurities, is very refractory, and is called *fireclay* (e.g., Stourbridge clay). This is made into refractory bricks, and to prevent undue contraction on firing,



broken firebricks ('grog') are added to the clay before heating. Graphite may also be incorporated with the fireclay when it is formed into crucibles. The earthenware body formed by firing without previous application of glaze is porous and is called *biscuit*. It then requires glazing. The *glaze* is a glassy surface



FIG. 362.—POTTERY KILNS.  
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imparted to the porous body and intimately united with it. Table-ware is usually lead glazed: the biscuit is spread over with a paste ('slip') composed of lead oxide with borates and silicates, together with clay and felspar. The whole is dried and re-fired at a somewhat lower temperature, when the glaze melts. Tin, antimony and zirconium oxides are sometimes added to glazes. In some cases the glaze may be put on the clay body before

firing, when the process is completed in one operation without first making a biscuit ware. Earthenware drainpipes and cheaper goods are **salt-glazed**: common salt is thrown into the furnace and the vapour of the salt is decomposed by the water vapour present, hydrochloric acid escapes and the alkali forms a thin layer of fusible silicate on the surface of the ware. **Porcelain**, made from a mixture of pure China clay and a material containing silica, is glazed with a mixture of finely-ground felspar, quartz, and gypsum.

The ware may be *painted* before glazing (some colours are applied on the glaze); the colours are metallic oxides (*e.g.*, cobalt oxide), which form coloured glasses (p. 595) with the glaze, or with lead oxide and silica, or borax, applied with the colouring oxide, before the glaze is applied. In porcelain used in laboratories the glaze must adhere firmly to the body, and the thermal expansions be so adjusted that no tendency to separation occurs on heating.

**Ultramarine.**—The rare mineral *lapis lazuli*, which has a beautiful blue colour, is a sodium-aluminium silicate containing sulphur in some form not completely defined, but probably as sodium sulphide. Ancient Egyptian amulets of this stone (which is very soft) are common. In 1826, Guimet obtained artificial *lapis lazuli*, or **ultramarine**.

A mixture of kaolin, soda ash, sulphur, and charcoal or resin is heated to bright redness in a closed crucible. A **white ultramarine**, or, if air has been admitted, a **green ultramarine** is produced. If this is mixed with powdered sulphur and heated in air, blue ultramarine is formed, which is ground and washed.

Alkalies are without action on ultramarine, so that it can be used in laundering to give a white appearance to linen, as it is not attacked by soap or soda. Acids, however, rapidly decompose it, with evolution of sulphuretted hydrogen.



## CHAPTER XXXIV

### COPPER, SILVER, AND GOLD

#### COPPER

**Copper.**—This metal occurs in the native or metallic state, and many of its ores are easily reduced ; it was therefore used in very early times, the oldest specimens of cast copper from Egypt dating to about 4000 B.C. It appears later in the form of the alloy bronze, which contains copper and tin. Working in bronze was practised by the Sumerians in 3500 B.C., and at least as early as 2500 B.C. in Egypt.

Copper was obtained by the Greeks and Romans from the island of Cyprus ; the Latin name *aes cyprium*, or Cyprian copper, afterwards became *cuprum*. These names, with the Greek *chalkos*, were also used for brass and bronze, so that many mistakes have been made in translating Greek and Latin texts, and in the Authorised Version of the Bible we read even of *brass* (an alloy of copper and zinc) being dug out of the earth ! 'Brass' is frequently used in the Bible when copper or bronze is meant, the word in the Greek version being *chalkos*. The metal was very early associated with the planet Venus, and designated by the symbol ♀.

*Native copper* occurs in large quantities near Lake Superior. Cuprous oxide,  $\text{Cu}_2\text{O}$ , and compounds of the carbonate and hydroxide occur native : *malachite*,  $\text{CuCO}_3, \text{Cu}(\text{OH})_2$ , and *azurite* (or *chessylite*),  $2\text{CuCO}_3, \text{Cu}(\text{OH})_2$ , are bright green and deep blue in colour, respectively, and are used in works of art. In combination with sulphur, copper is widely distributed. The commonest ores are *copper pyrites*,  $\text{CuFeS}_2$ , and *peacock copper* (or *variegated copper ore*),  $\text{Cu}_3\text{FeS}_3$ , i.e., sulphides of copper and iron. Copper is extracted from the residues left after burning iron pyrites containing copper (*cupreous pyrites*), in the manufacture of sulphuric acid.

Copper occurs in the red colouring matter of the feathers of the touraco bird, and in the *haemocyanin* of the blood of the cuttlefish, which acts like haemoglobin (p. 425) as an oxygen carrier, but

is blue in arterial and colourless in venous blood. Minute quantities occur in plants, especially in green peas.

The main copper-producing countries are the United States, Rhodesia, Chile and Canada, and the normal annual world production is about  $1\frac{1}{2}$  million tons. The commercial metal is of a high degree of purity and is used for electrical conductors and for alloys.

**Metallurgy of copper.**—The *oxide* and *carbonate ores* are simply roasted and the oxide formed is smelted with coal :

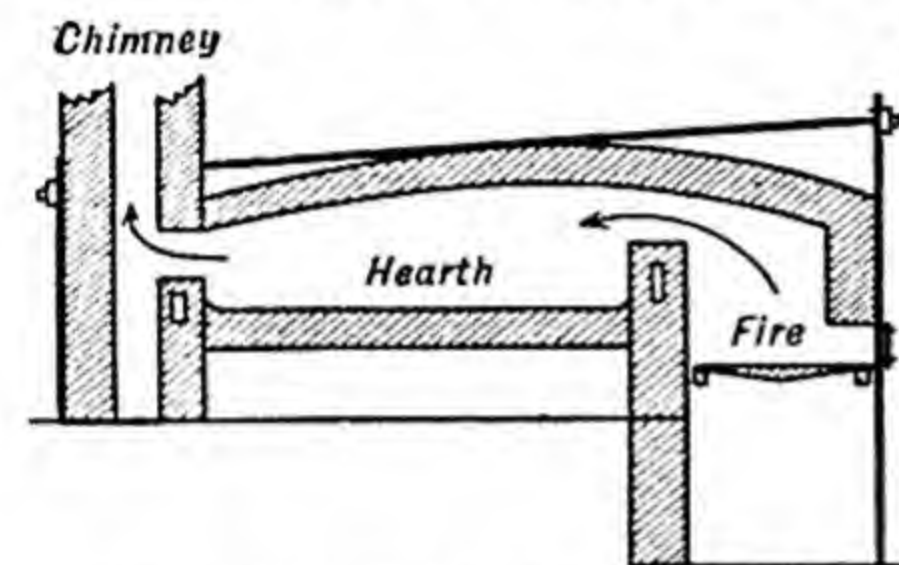
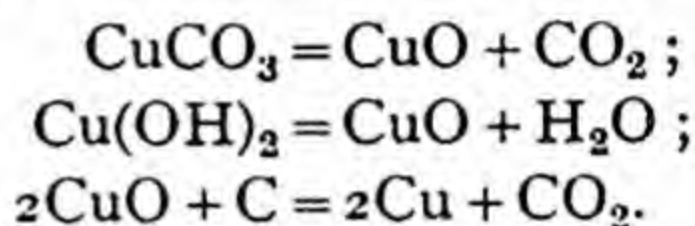
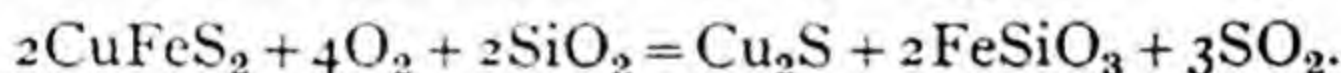


FIG. 363.—REVERBERATORY FURNACE.

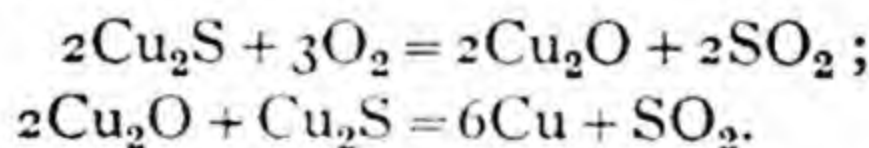


*Sulphide ores* are more difficult to reduce. They are first roasted in a reverberatory furnace (Fig. 363) in contact with air, when the iron is principally oxidised and

forms a slag of ferrous silicate with added silica, whilst the copper remains in combination with sulphur as cuprous sulphide,  $\text{Cu}_2\text{S}$ , which fuses and sinks below the slag :



The cuprous sulphide is separated and again heated in air. Part of the cuprous sulphide is then converted into oxide, and this reacts by 'self-reduction' with the remaining sulphide to form crude metallic copper :



The ore is found mixed with silicate *gangue*, which is separated mechanically and by froth-flotation. The mixture of ore and gangue is crushed, and suspended in water to which a little acid or alkali is added, and about one lb. of pine oil, tar oil, or eucalyptus oil per ton of ore. A blast of air is sent through the liquid, when a froth of fine bubbles is produced. The *ore particles*, which are preferentially wetted by the oil, pass off with the froth, the particles of ore coating each bubble of air, which in turn is surrounded by a film of oil. The earthy *gangue particles*, which are preferentially wetted by the water, do not



rise with the froth. The froth is then broken down mechanically and the ore smelted.

In the American smelting process, the ore is roasted, and fused in a reverberatory furnace with limestone; the fused *matte* of sulphides of iron and copper is then run into a Bessemer converter (Fig. 364; cf. Fig. 369) and 'blown,' i.e., a blast of air is sent through the fused material. The iron is oxidised and

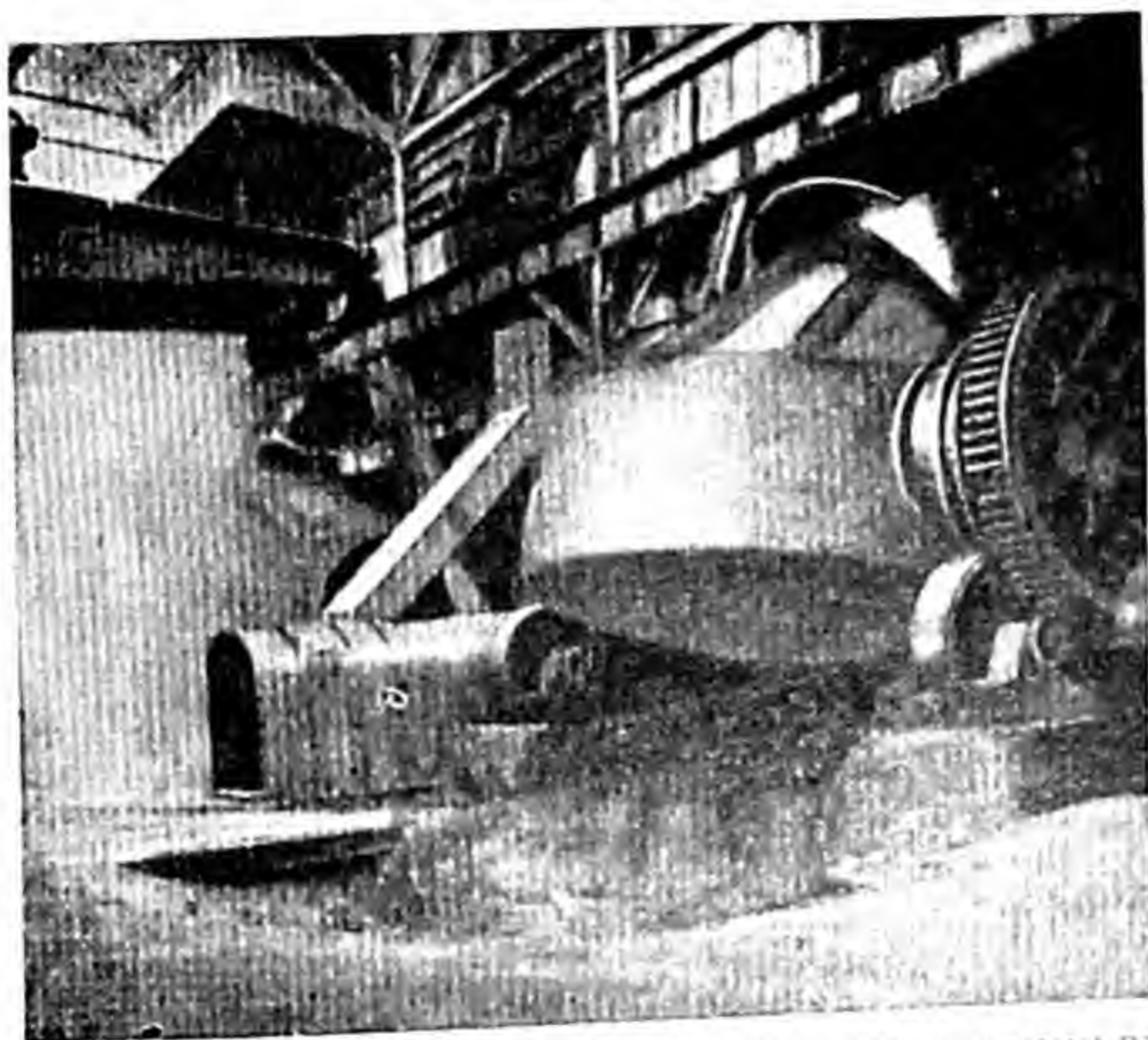


FIG. 364.—' BLOWING ' COPPER IN A BESSEMER CONVERTER.

forms a slag with silica added, and the copper sulphide is converted into metal by the reactions given above.

Crude copper is first purified by *paling*; it is fused and a pole of green wood thrust into the metal. Torrents of reducing gases are evolved, which convert any oxide present into metal. It is further refined by electrolysis.

**Copper refining.**—Copper is largely used in the manufacture of wires (e.g., telegraph wires) and cables for carrying electric currents, and since its conductivity is appreciably lowered by traces of impurities, it is necessary to use a highly purified metal. The traces of silver and gold found in the crude metal are also

of value. In refining copper, the electrolytic process is exclusively used; the thin slabs of crude metal are immersed in a bath of copper sulphate solution acidified with sulphuric acid, and made the positive electrodes, or anodes. The cathodes consist of thin sheets of pure copper (Fig. 365). The copper dissolves from the anode as cupric ions,  $\text{Cu}^{++}$ , and these travel to the cathode, where they are deposited as pure copper. Iron and zinc pass into solution as sulphates; gold and silver (with some impurities) fall to the bottom as an *anode slime*, which is collected for the purpose of obtaining the precious metals. The electrolytic copper is then melted and cast.

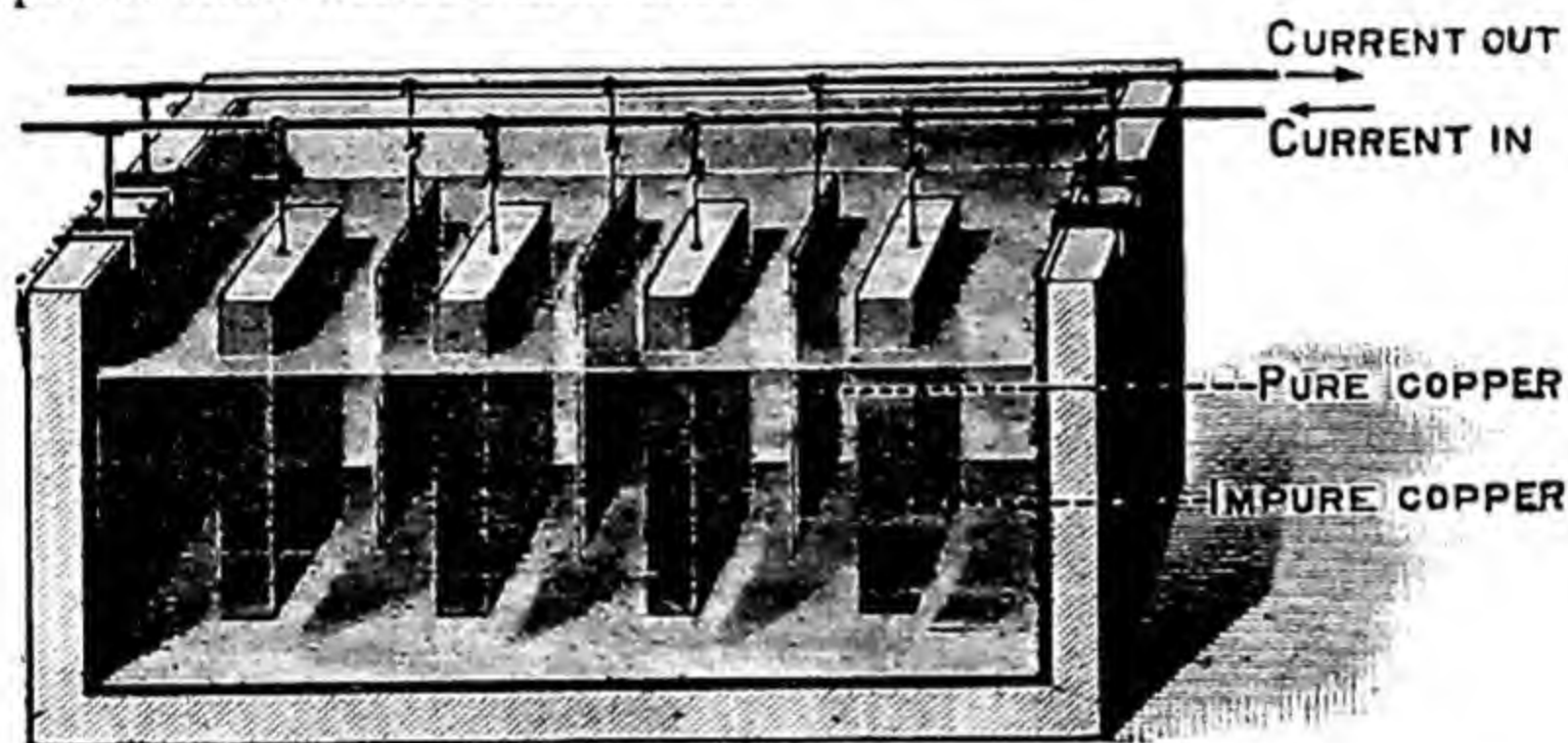


FIG. 365.—REFINING COPPER.

A similar process has been used since its invention by Jacobi in 1837, in *electrotyping*, *i.e.*, depositing copper electrolytically. This is used in reproducing statues and other works of art. The copper may be deposited on plaster casts covered with graphite to render them conducting, and the shell stripped off. In the same way, if an impression is taken on gutta percha or wax, and the latter covered with powdered graphite to render it conducting, a deposit of copper may be formed which reproduces the shape of the original object.

**Properties of copper.**—Copper has a characteristic red colour, which is pale when the metal is very pure. It is very malleable and ductile, and can be rolled into sheets, hammered into thin leaves, and drawn into wire. The metal may also be 'spun' on the lathe, in the production of seamless vessels. Small quantities of impurities reduce the malleability of the metal.

Copper is used for the driving bands of steel projectiles. The driving band consists of a copper band recessed into a groove in the base of the shell, and projecting slightly above the surface



of the latter so as to be somewhat larger than the bore of the gun. On firing the shell, the copper is squeezed into the spiral rifling of the gun barrel, and the gases are prevented from escaping, whilst the shell acquires a rotation which serves to keep it in its trajectory without turning over.

In pure dry air copper does not oxidise, but in ordinary moist air the metal rapidly tarnishes and becomes covered with a brown film, gradually turning green to a *patina* which is usually the basic sulphate,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ , or near the sea the basic chloride,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ . This film, unlike iron rust, protects the copper from corrosion. *Clean* (polished) copper utensils are safely used in cooking, except with acid fruits, vinegar or much common salt, but when corroded may render food poisonous. Tinned copper is safer, but aluminium vessels are now largely used.

Important alloys of copper are **bronze**, composed of copper and tin, and **brass**, composed of copper and zinc. Common bronze contains about 90 parts of copper and 10 of tin; the metal used for coinage contains 95 of copper, 4 of tin and 1 of zinc. Common brass consists of two parts of copper to one of zinc. **German silver** contains copper, zinc, and nickel; **bell metal** consists of four or five parts of copper to one of tin.

The melting point of copper is rather high, viz.  $1083^\circ$ , but it is lower than that of iron ( $1533^\circ$ ). Its specific gravity of 8.9 is lower than that of lead (11.4) but higher than that of iron (7.9). Brass and bronze are more fusible than pure copper and make better castings.

Brass and copper articles are often *lacquered* to prevent corrosion: the lacquer is a solution of shellac in spirit, coloured with the gum resin called dragon's blood, and deposits an impervious film on the metal. Nitrocellulose varnishes are now replacing lacquer.

On heating in air, the metal is readily oxidised, and the product forms scales which are black on the outside (cupric oxide,  $\text{CuO}$ ), but are red on the side which was in contact with the metal (cuprous oxide,  $\text{Cu}_2\text{O}$ ). If heated for a long time in air, cupric oxide is formed.

These two oxides correspond with the cuprous and cupric salts, in which copper is respectively univalent and bivalent.

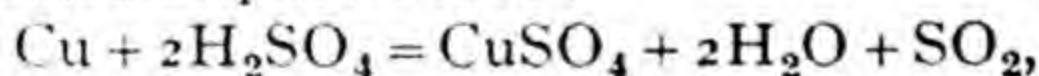
CUPRIC COMPOUNDS,  $\text{CuX}_2$ 

**Cupric oxide.**—Cupric oxide, or *black oxide of copper*,  $\text{CuO}$ , is formed by the prolonged heating of the metal in air or oxygen, or by heating cupric nitrate:  $2\text{Cu}(\text{NO}_3)_2 = 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$ . It is a black solid which is stable up to its melting point. Cupric oxide is readily reduced by hydrogen, carbon, or organic substances, when heated below redness, and the metal remains. The oxide dissolves in fused borax, colouring it blue or green. If a little tin or stannous chloride is added to the borax bead, the cupric oxide is reduced to cuprous oxide, which forms an opaque red bead. Cupric oxide is used to give a light blue colour to glass.

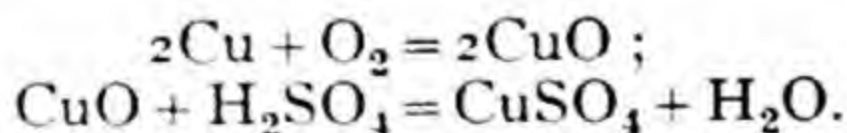
**Cupric hydroxide**,  $\text{Cu}(\text{OH})_2$ , is formed as a light blue precipitate on adding potassium or sodium hydroxide, or ammonia, to a solution of a cupric salt, *e.g.*, copper sulphate. It is insoluble in excess of dilute potassium or sodium hydroxide but dissolves in excess of ammonia, forming a deep blue solution containing the ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . On boiling with water, cupric hydroxide becomes black from conversion into cupric oxide, this change being complete when the dry precipitate is heated to redness.

Cupric oxide is a basic oxide and dissolves in dilute sulphuric, hydrochloric, and nitric acids to form solutions of cupric sulphate, chloride, and nitrate, respectively.

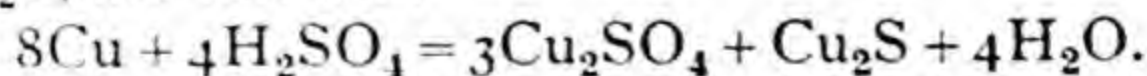
**Cupric sulphate.**—The commonest cupric salt is the sulphate,  $\text{CuSO}_4$ , commonly known simply as *copper sulphate*. This crystallises from water in large blue glassy crystals,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , called *blue vitriol* or *bluestone*. Copper sulphate is obtained by dissolving cupric oxide in dilute sulphuric acid, by heating copper with concentrated sulphuric acid:



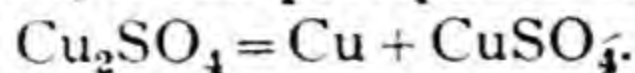
and by the action of hot dilute sulphuric acid on copper in presence of air:



The action of hot concentrated sulphuric acid on copper is really rather complicated. Cuprous sulphate,  $\text{Cu}_2\text{SO}_4$ , and cuprous sulphide,  $\text{Cu}_2\text{S}$ , are formed:

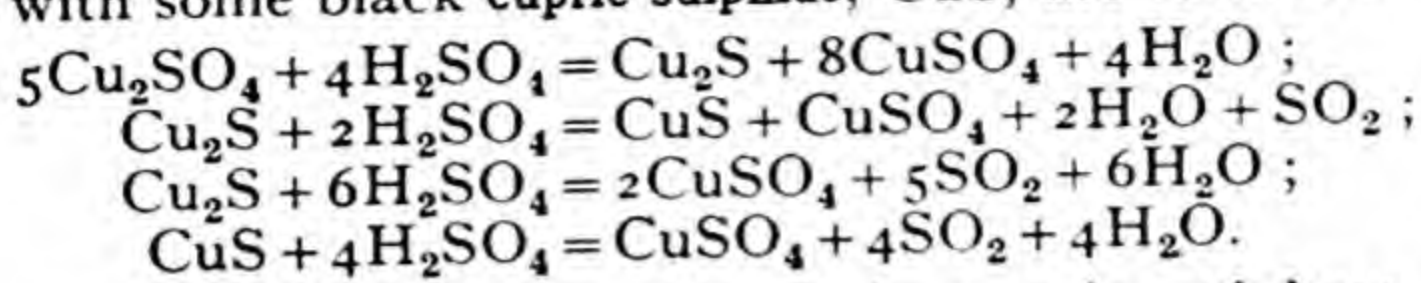


When the solution at this stage is filtered through asbestos and diluted with water, a red precipitate of copper is obtained:



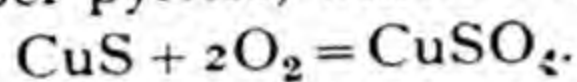


As the reaction proceeds both the cuprous sulphate and cuprous sulphide are decomposed by the sulphuric acid and cupric sulphate with some black cupric sulphide,  $\text{CuS}$ , are formed :

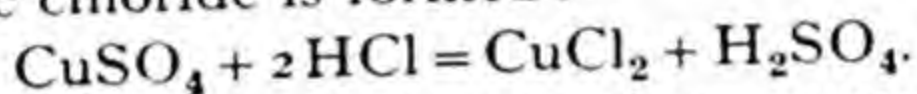


The final products are almost entirely cupric sulphate and sulphur dioxide, although a *little* black cupric sulphide may escape reaction.

Copper sulphate is also prepared on the large scale by the 'weathering' of copper pyrites, which may first be roasted :



When hydrogen chloride gas is passed over heated copper sulphate, cupric chloride is formed :



Commercial cupric sulphate sometimes contains ferrous sulphate, with one hydrated form of which,  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ , it is isomorphous and forms mixed crystals. A solution of the salt is used for steeping seeds to prevent 'smut,' a fungus growth.

The following concentrations of salts, one part in the given proportion of water, have an injurious effect on wheat seedlings when applied to the roots :

Copper sulphate	-	700,000,000
Mercuric chloride	-	30,000,000
Silver	- - -	1,000,000
Zinc sulphate	-	40,000
Borax	- - -	1,000
Calcium chloride	-	260

The great activity of copper salts is apparent.

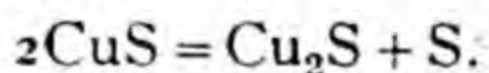
The differential or selective poisoning of weeds by the use of solutions which do not injure the crop is utilised in killing charlock or wild mustard in barley or oat fields by spraying with 40-70 gallons per acre of a 3 per cent. solution of blue vitriol, when the charlock withers and dies, while barley, oats, and clover are not injured. 'Lawn sand,' for destroying plantains and daisies in lawns, is sand containing ammonium sulphate, applied in March, when the ammonium salt kills the weeds but acts as a fertiliser to the grass, although it may brown it temporarily. Slugs are killed by sprinkling them with a mixture of powdered alum and sand. Ordinary 'weed killer' is a solution of sodium

arsenite, also used for sheep dipping. It is made by dissolving arsenious oxide ( $\text{As}_2\text{O}_3$ ) in caustic soda solution.

A mixture of copper sulphate solution and milk of lime, containing suspended basic cupric sulphate, is used for spraying plants to prevent the growth of fungi and is called *Bordeaux mixture*. A common mixture contains 6 lb. of copper sulphate and 6 lb. of quicklime in 50 gallons of water.

Copper sulphate is employed in calico printing, in the preparation of pigments (*e.g.*, *Scheele's green*,  $\text{Cu}_3(\text{AsO}_3)_2 \cdot 2\text{H}_2\text{O}$ ), and in electro-deposition. The salt is insoluble in alcohol; it is precipitated in small crystals when alcohol is added to the aqueous solution. On heating the blue pentahydrate crystals at  $100^\circ$  they crumble to a bluish-white powder of monohydrate,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . At  $220^\circ$ - $260^\circ$  this loses most of the combined water. The last molecule of water of crystallisation of a salt is often retained much more tenaciously than the others. The white powder obtained by dehydration is used in the detection of traces of moisture in alcohol, ether, etc., since it very readily absorbs water and becomes blue in colour.

**Cupric sulphide.**—Cupric sulphide,  $\text{CuS}$ , is a black solid formed by heating copper powder with *excess* of flowers of sulphur to a temperature below  $440^\circ$ , or, more easily, by precipitating an acid solution of a cupric salt with hydrogen sulphide. In the moist state it is rapidly oxidised by air, forming a blue solution of the sulphate. Cupric sulphide is less stable than cuprous sulphide, and loses sulphur when strongly heated alone, or in hydrogen:



The product usually obtained by heating copper with sulphur is *cuprous* sulphide, not cupric sulphide.

**Cupric nitrate.**—This salt is prepared by dissolving the metal, oxide, or carbonate in dilute nitric acid, and on evaporation forms blue, deliquescent crystals,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . Copper nitrate possesses powerful oxidising properties: if a few crystals are moistened and wrapped in tinfoil, sparks are emitted.

**Cupric chloride.**—This salt is obtained in the anhydrous form as a dark brown mass by burning copper in excess of chlorine, or by heating the hydrate,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . When strongly heated it loses chlorine and leaves cuprous chloride. A crystalline hydrate,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , is formed in emerald-green crystals by dissolving cupric oxide in concentrated hydrochloric acid and evaporating. In concentrated solutions it is yellowish-green; on adding



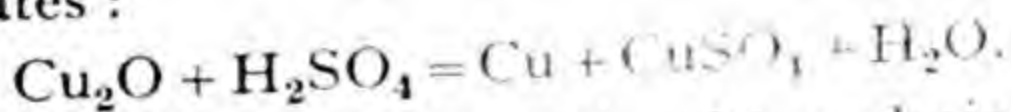
concentrated hydrochloric acid the colour becomes yellow. This is due to the reversal of the ionisation:  $\text{CuCl}_2 \rightleftharpoons \text{Cu}^{++} + 2\text{Cl}'$ , the colour of the undissociated salt being yellow. A very dilute solution shows the pure blue colour of the cupric ion,  $\text{Cu}^{++}$ ; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised salt. Cupric chloride is very deliquescent, and is also soluble in alcohol. The alcoholic solution burns with a fine green flame. A green flame is also formed by heating a little cupric oxide moistened with hydrochloric acid on a platinum wire in a Bunsen flame.

An oxychloride of copper is prepared for use as a pigment, by boiling copper sulphate solution with a small quantity of bleaching powder.

**Cupric carbonates.**—Only *basic* carbonates of copper are known; the most important are the minerals *chessylite* (or *azurite*),  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (deep blue), and *malachite*,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (bright green). Azurite dissolves in a hot solution of sodium bicarbonate; on boiling the solution, malachite is deposited. Sodium carbonate precipitates from a solution of a copper salt a light blue basic carbonate of copper.

#### CUPROUS COMPOUNDS, $\text{CuX}$

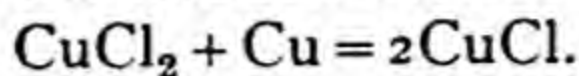
**Red cuprous oxide**,  $\text{Cu}_2\text{O}$ , is formed by the partial reduction of cupric compounds in the presence of alkalis. If Rochelle salt (sodium potassium tartrate) is added to a solution of cupric sulphate, the mixture does not give a precipitate of cupric hydroxide on addition of excess of caustic soda but forms a deep blue liquid called **Fehling's solution**. When this is boiled with glucose (p. 494) a red precipitate of cuprous oxide,  $\text{Cu}_2\text{O}$ , is formed by the reducing action of the glucose. Cuprous oxide is also formed (mixed with cupric oxide) by heating copper in a limited supply of air. When fused with glass it forms *ruby glass* (p. 595). With dilute sulphuric acid it gives *cupric* sulphate, and metallic copper separates:



Dilute nitric acid dissolves the oxide with evolution of oxides of nitrogen, and a solution of *cupric* nitrate is formed. Concentrated hydrochloric acid dissolves cuprous oxide with formation of a solution of *cuprous* chloride,  $\text{CuCl}$ .

**Cuprous chloride**,  $\text{CuCl}$ , is most easily prepared by dissolving cuprous oxide in concentrated hydrochloric acid, or by reducing

cupric chloride by boiling a solution in hydrochloric acid with copper turnings until the solution becomes colourless :

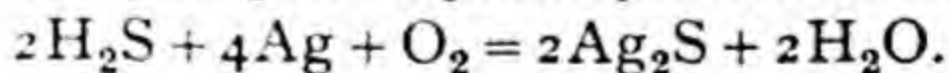


When the solution is poured into water a white precipitate of cuprous chloride is formed. This is rapidly washed and dried out of contact with air. Moist cuprous chloride easily oxidises on exposure to air. It is soluble in ammonia and the solution absorbs carbon monoxide and acetylene, the latter giving a red precipitate of  $\text{Cu}_2\text{C}_2$ .

A black brittle mass of cuprous sulphide,  $\text{Cu}_2\text{S}$ , forms when copper burns in sulphur vapour. A few pieces of roll sulphur are placed on the bottom of a small flask, and the lower half filled with copper turnings. On heating the flask, the copper glows with a red light, and a black mass of cuprous sulphide is formed. This is the stable sulphide of copper. When moistened with water and exposed to air it oxidises slowly to a blue solution of cupric sulphate.

### \*SILVER

**Silver.**—Silver has been known from the earliest times (p. 14); its association with the moon led to the name Luna, or Diana, given to it by the alchemists, who represented it by the symbol of the crescent moon, ☾. It is not oxidised by pure air or oxygen, either in the cold or when heated, and is an example of a noble metal (silver, gold, platinum). In ordinary air it slowly tarnishes, and becomes covered with a thin adherent film, which exhibits the colours, yellow, blue, and black, with increasing thickness. This film is composed of silver sulphide,  $\text{Ag}_2\text{S}$ , formed by the decomposition of hydrogen sulphide present in the air :



Silver spoons become black in contact with eggs, the albumin of which contains combined sulphur.

Most of the silver used is produced by **desilverising** lead, obtained from galena (*q.v.*), which contains small amounts of silver. *Old* lead roofs often contain appreciable amounts of silver. The lead is melted with zinc, which dissolves the silver and floats to the surface.

Silver is a white, very ductile and malleable metal, used for coinage, jewellery, and decorative purposes. It melts at a lower temperature ( $960^\circ$ ) than copper and has a higher specific gravity (10.5). *Standard silver*, in Great Britain, contains 925 parts of



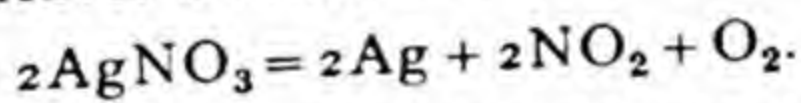
silver and 75 of copper in 1000 parts. Modern silver coinage is considerably debased, containing only about half its weight of silver.

Brass and copper articles are plated with silver by deposition by electrolysis from a solution of a silver salt containing cyanide, with an anode of silver. Glass mirrors are generally silvered by depositing the metal on them from a silver solution containing caustic potash, ammonia, and a reducing agent, such as formaldehyde. Old mirrors were generally backed with tin amalgam.

The most important salt of silver is the **nitrate**,  $\text{AgNO}_3$  (*lunar caustic*), prepared by dissolving the metal in dilute nitric acid and crystallising. It is used as a reagent, giving a white precipitate of **silver chloride**,  $\text{AgCl}$ , with chlorides, insoluble in dilute nitric acid but readily soluble in ammonia. Bromides give a pale yellow **silver bromide**,  $\text{AgBr}$ , insoluble in dilute nitric acid and only sparingly soluble in dilute ammonia, and iodides give a yellow precipitate of **silver iodide**,  $\text{AgI}$ , insoluble in nitric acid and ammonia. Since tap-water always contains chlorides, it gives a turbid solution with silver nitrate.

**Silver oxide**,  $\text{Ag}_2\text{O}$ , is a brown powder precipitated on the addition of caustic soda to silver nitrate solution. When heated it evolves oxygen and leaves metallic silver.

When *strongly* heated, silver nitrate evolves nitrogen peroxide and oxygen and leaves a residue of metallic silver :



Silver nitrate is used as a *caustic* (*lunar caustic*), for which purpose it is fused with some potassium nitrate and cast into sticks. It leaves a deep black stain on the skin owing to reduction to finely divided silver, which appears black. It is used in making ink for marking linen, when the same black deposit of silver is formed.

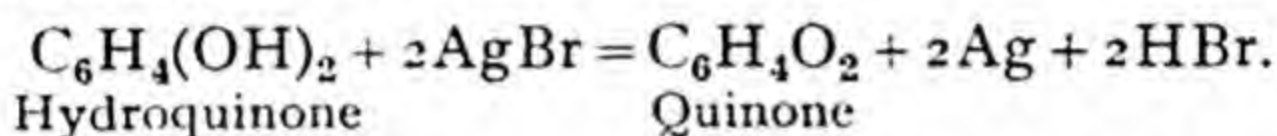
**Photography.**—The blackening of silver chloride on exposure to light was observed by Boyle. Scheele (1777) showed that if the blackened substance is digested with ammonia, unchanged silver chloride is dissolved and a residue of silver remains. He also noticed that the violet rays act most strongly on the chloride, whilst the red and orange rays have practically no action. Silver salts may be rendered sensitive to these rays by adding to them certain dyes (aurin, erythrosin, cyanines) which absorb light of these wave-lengths, and are called **photo-sensitisers**.

The sensitive silver salts were used in making light pictures, or **photographs**, by Davy and Thomas Wedgwood (1802).



In the modern process an emulsion of silver bromide is prepared by adding silver nitrate to a solution of gelatin in hot water containing potassium bromide. The warm emulsion, after 'ripening' for some time, when the silver bromide grains increase in size, is allowed to cool and set. The jelly is cut up, washed with water to remove soluble salts, and is then remelted and poured in a thin film on glass (for 'plates') or celluloid (for 'films'). It is then dried. All operations are carried out in the dark or in orange light, to which silver salts are not sensitive.

After exposure in the camera, which may be for only a small fraction of a second, the film or plate does not change in appearance, but in reality a change has occurred in the places on which light has fallen. It is *developed* by immersing in a solution of a reducing agent, such as pyrogallol, hydroquinone or metol, in presence of alkali. The *altered* silver bromide is then reduced to black metallic silver :



To prevent over-vigorous development, when some of the unchanged bromide is reduced and leads to 'fogging' of the plate, a *retarder*, consisting of potassium bromide, is added to the developer.

*Desensitisers* are dyes (usually of the safranine class) which when dissolved in the developer solution enable development to be carried out in ordinary light instead of in the photographic dark room.

After washing, the plate is *fixed* in sodium thiosulphate, which dissolves out all silver salts. The print, or positive, is made on paper impregnated with silver chloride and coated with albumin, which is *toned* after exposure by immersion in a solution of gold chloride (brown tone), or potassium platinochloride (grey tone), a little of the silver being dissolved and replaced by the nobler metal. It is then fixed in thiosulphate.

A print may also be made on silver bromide and chloride paper (*gaslight paper*), which is exposed and developed in the same way as a plate. The gelatin in the plate and the albumin on the paper act as *sensitisers* to the silver salt, accelerating the action of light upon it.

Sheppard (1925) found that the very high speed of photographic emulsions is due to the presence of traces (1 part in 100,000 to 1 part in 300,000) of organic sulphur compounds present in



gelatin. He considers sensitisation to be due to the formation of 'sensitive centres' by the conversion of these sulphur compounds into silver sulphide by reaction with silver halide. This discovery has altered many of the theories of photography, but the subject is still very empirical.

### \*GOLD

**Gold.**—Gold, by reason of its occurrence in the free state, and of its beautiful colour and brilliance, was one of the first metals known to man. Gold ornaments are found in neolithic remains. The metal was associated with the sun, was called *Sol*, and represented by the symbol ☉, or ☿. The alchemists considered that the other metals, if suitably purified, or 'cleansed,' could be transmuted into gold.

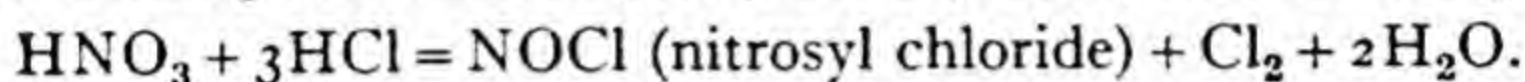
Gold occurs usually in the native condition, alloyed with a certain amount of silver, and sometimes copper and traces of platinum. Some traces of gold are found in pyrites and other ores, and in sea water. Gold is recovered from burnt pyrites, but a seaweed which collects gold instead of iodine is yet unknown. The native gold occurs in quartz veins or reefs. Gold occurs in many places in Europe, and all over Asia. The Russian mines of the Urals, opened in 1819, supplied most of the metal until the accidental discovery of gold in California in 1849. The richest fields are in Africa, especially the Transvaal Rand, which give the highest production in the world, and in Australia. In North America the fields extend from Mexico to Klondike.

Pure gold is too soft for use as ornaments or for coinage, and it is alloyed with copper, or silver, or both. The copper makes the colour redder (English gold coin), silver imparts a pale colour (Australian gold coin). The ancient *asem*, *electrum*, or 'pale gold,' was an alloy of gold and silver. The *fineness* is expressed either in parts per 1000, or in *carats*, pure gold being 24 carat fine, and five standard alloys of 22, 18, 15, 12, and 9 carat, *i.e.*, parts of gold in 24 of alloy, are legalised. English gold coin is 22 carat; German, Italian, and American coinage is 21.6 carat.

**Gold plating** is carried out in the same way as silver plating, by electro-deposition from solutions of gold cyanide in potassium cyanide, the requisite amounts of silver and copper salts being added. These metals are deposited as an alloy with the gold.

Gold is the most ductile metal, as was stated by Pliny, and can be beaten into leaves 0.00009 mm. thick. The deposits on gold lace are only 0.000002 mm. thick. By treating gold leaf with a solution of potassium cyanide, films 0.0001 mm. thick are obtained. A piece of gold leaf pressed between two plates of glass will transmit a green light.

Gold is insoluble in single acids, but it dissolves in a mixture of nitric and hydrochloric acids, called *aqua regia* (because it dissolves gold, the 'king' of metals). The hydrochloric acid is oxidised by the nitric acid to chlorine, which dissolves the gold, forming gold chloride (really  $\text{AuCl}_3$ ,  $\text{HCl}$ , *i.e.*,  $\text{HAuCl}_4$ ) :



Aqua regia also dissolves the metal **platinum**, forming platinic chloride (really,  $\text{PtCl}_4 \cdot 2\text{HCl}$ , *i.e.*,  $\text{H}_2\text{PtCl}_6$ ). Platinum belongs to the transitional elements (p. 236) : it has a high melting point and is not attacked by common reagents, so that it is used in the laboratory for wire, crucibles, and dishes. On the large scale platinum, a very expensive metal, is chiefly used as a catalyst (p. 356), and (alloyed with iridium) for the make-and-break contacts in magnetos and induction coils.



## CHAPTER XXXV

### IRON

**Iron.**—The present day is in the Age of Iron, the most important and useful of the metals. Iron did not come into general use until about 1800 B.C., whilst bronze was used for weapons and implements as early as 2500 B.C. Even Homer refers to iron as a rarity, although he is probably speaking of the Mykenean age which preceded his own, and finds of iron are very rare in that period. Iron is said to have been used at an early date in China, and 'Indian iron' was famous in the Roman period.

Iron does not occur to any great extent in the free state on the earth, although meteorites consist of metallic iron with some nickel. Meteorites may also consist partly of stony and of glassy minerals. On account of the presence of nickel, meteoric iron does not easily rust in moist air. Meteoric dust, consisting chiefly of iron, is constantly falling on the earth from space, although its presence is only noticed on the surface of the otherwise unsullied snows of the polar regions. Large masses of native iron, which may be of meteoric origin, or have been derived from the reduction of ores by burning coal deposits, occur in a few places, *e.g.* in Greenland. Iron is contained in the soil, in green plants, and in the hæmoglobin or red colouring matter of the blood. Iron compounds also occur plentifully as minerals, but not all these are suitable for the extraction of the metal, since they may contain impurities which would pass into the iron and render it useless. Iron pyrites,  $\text{FeS}_2$ , for instance, is not an ore of iron, but is used for the manufacture of sulphuric acid (p. 361).

The common ores of iron are **oxides**, such as **ferrosoferric oxide**, or **magnetite**,  $\text{Fe}_3\text{O}_4$  (so called because some varieties are naturally magnetic), which provides the very good Swedish iron; **ferric oxide**,  $\text{Fe}_2\text{O}_3$ , occurring as **hæmatite**, or hydrated as **limonite** or (with impurities) as **bog-iron ores**; and **ferrous carbonate**,  $\text{FeCO}_3$ ,

**The metallurgy of iron.**—Commercial varieties of iron, *viz.* cast iron, wrought (or malleable) iron and steel are obtained from the ores in the following order :

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Ore  $\rightarrow$  Cast, or Pig-iron  $\rightarrow$  Wrought iron  $\rightarrow$  Crucible Steel.

The extraction of iron from the ore involves the following processes :

(1) Preliminary roasting, or calcination, to drive off carbon dioxide and moisture and leave ferric oxide,  $\text{Fe}_2\text{O}_3$ .

(2) Smelting, or reducing the ore with carbon in the blast furnace.

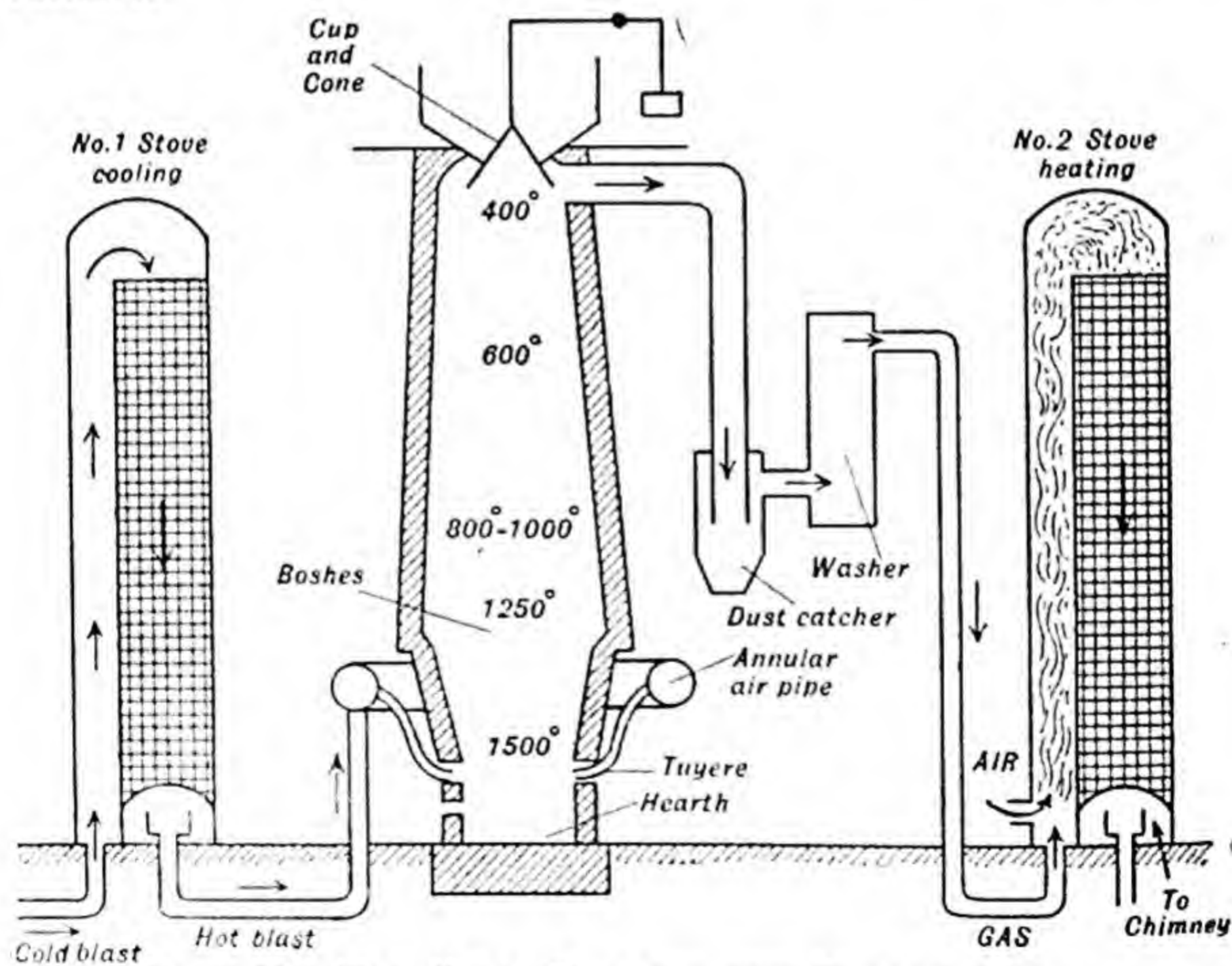


FIG. 366.—THE BLAST FURNACE AND COWPER STOVES.

The blast furnace, introduced about 1500 (Fig. 366) consists of an outer shell of steel plates, lined with refractory bricks. It is about 75 ft. high, the greatest width being about 24 ft. (at the

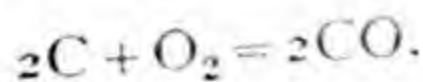


'boshes'). The mouth is closed with a *cup-and-cone*, through which a mixture of ore, limestone and fuel is fed into the furnace, whilst the gases (carbon monoxide and nitrogen) pass away through a pipe to a *dust-catcher* and a *washer*, and are utilised in heating the blast. The furnace below the *boshes* narrows gradually to a *hearth*, at the base, which is pierced with holes for the water-jacketed iron blowing pipes, or *tuyères*, through which air is forced from an annular pipe, by means of powerful blowing engines. The hearth is also pierced with a hole stopped with clay, from which the molten iron is periodically tapped into sand moulds on the ground, and a *slag notch* at a higher level, through which the molten slag runs continuously from above the fused metal.

Formerly, when charcoal was the fuel used in smelting iron, the industry was carried on in England in the Sussex Weald, where forests were cut down to provide the fuel, but when coal began to be used, the iron industry moved to the coal beds of the Midlands and North. The coal is nearly always converted into coke before use in the blast furnace, although in Scotland raw coal is used. The charge for the blast furnace consists of the requisite amounts of roasted iron ore, coke, and limestone (to form the slag). The process goes on continuously. A large blast furnace will use 1500 tons of ore, 1000 tons of coke, 500 tons of limestone and 4000 tons of air in a day and produce about 1000 tons of pig iron and 100 million cubic feet of gas containing about half its volume of nitrogen and the remainder carbon monoxide and carbon dioxide in about equal proportions by volume.

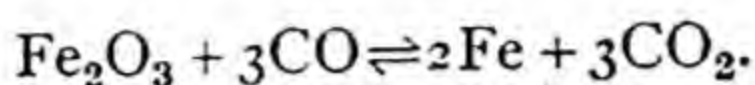
The air blast is *pre-heated* by passing the air through *Cowper stoves* (Fig. 366), consisting of tall iron cylinders lined with fire-bricks, packed on one side with chequer brickwork. Part of the hot gas from the blast furnace, together with sufficient air to burn it, passes through these until the bricks are heated to redness. The gas is then turned through a second stove and the air blast to the *tuyères* sent through the first one until the brickwork has cooled. The two stoves are thus alternately used as absorbers and emitters of heat, or as heat regenerators. In this way an economy of fuel is effected.

**Chemical reactions in the blast furnace.**—The oxygen of the blast unites with carbon in the hearth to produce carbon monoxide :



*The temperature of the charge passing down the furnace increases continually from the mouth to the hearth.*

Above the boshes, at a dull red heat, the ferric oxide is reduced by the carbon monoxide to spongy iron :



In this upper region the limestone is decomposed into quicklime and carbon dioxide, some of the latter being reduced to carbon monoxide by the heated carbon.

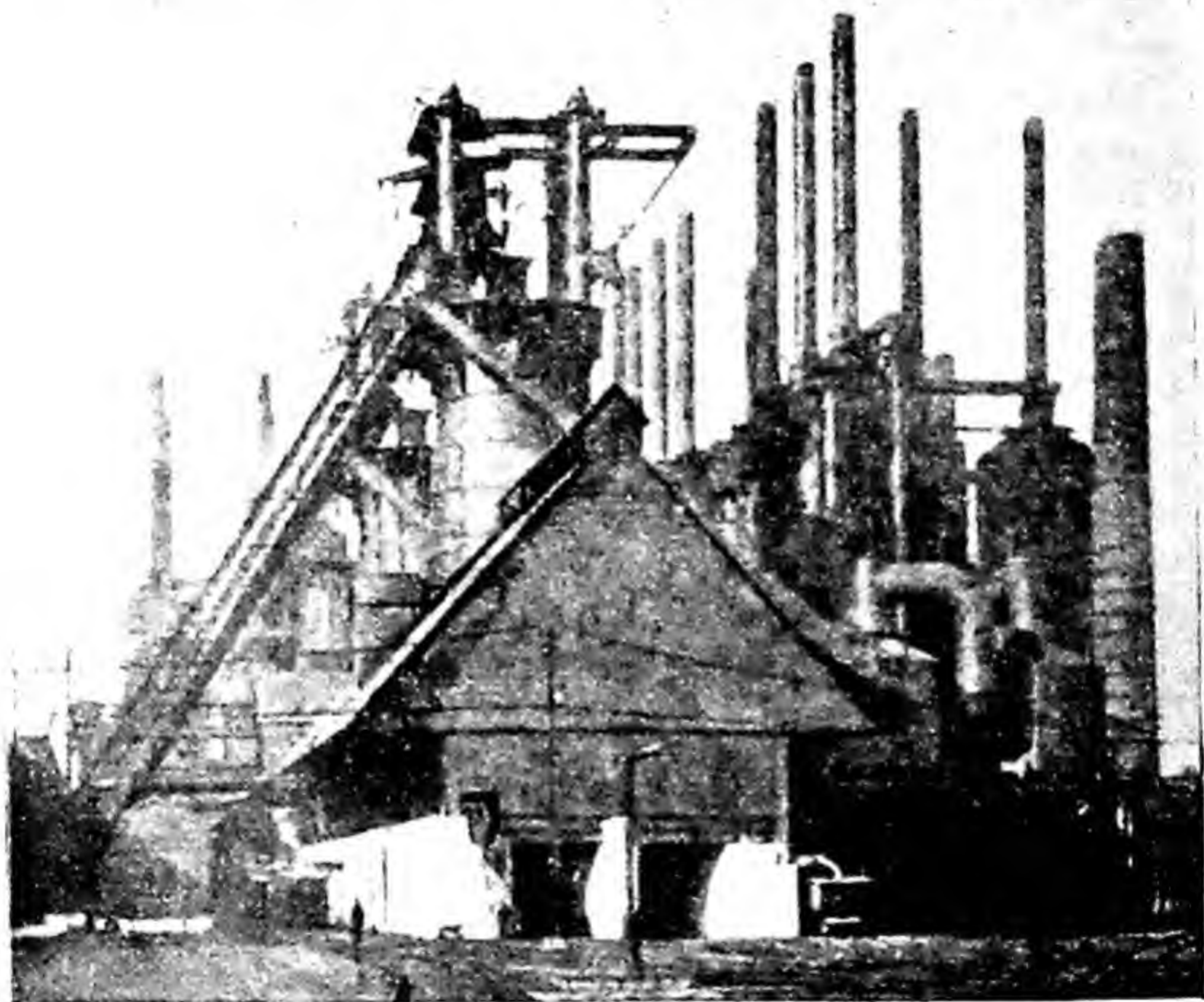


FIG. 367.—BLAST FURNACES WITH COWPER STOVES.

Near the centre of the furnace, down which the charge is passing continuously, finely divided carbon is deposited by decomposition of carbon monoxide :



and at the same time the lime,  $\text{CaO}$ , unites with the silica,  $\text{SiO}_2$ ,



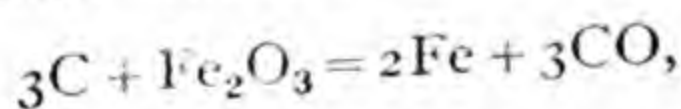
and alumina,  $\text{Al}_2\text{O}_3$ , of the ore to form a fusible **slag** consisting of calcium silicate and aluminate. This slag runs out of the lower part of the furnace through the *slag-notch*.

At a white heat, in the lowest part of the furnace, where the blast enters, the spongy iron, containing carbon, silicon, sulphur, and phosphorus (the last two being harmful impurities) melts, and is tapped off from time to time into sand moulds to form **cast iron** or **pig iron**, or else is sent in the fused state to the Bessemer or open-hearth steel furnaces.

**Cast iron.**—*Pig iron* contains from 3 to 4 per cent. or more of carbon, with silicon and manganese, and as impurities sulphur and phosphorus. When the cooling is rapid, *white pig iron* is formed, in which all the carbon is in the form of **iron carbide**,  $\text{Fe}_3\text{C}$ . It is brittle, coarsely crystalline, and dissolves nearly completely in dilute hydrochloric acid, evolving a mixture of hydrogen and hydrocarbons. If, however, the molten pig iron, containing silicon, is *slowly* cooled, most of the carbon separates in the form of fine laminae of *graphite*, the metal at the same time becoming softer and of a finer texture; on solution in hydrochloric acid it evolves chiefly hydrogen and leaves a black residue of graphite. This variety of cast iron is known as *grey pig iron*. An intermediate variety is called *mottled pig iron*.

Cast iron forms sharp castings since, like water (p. 297), it expands on solidification. Pig iron as it comes from the blast-furnace is the cheapest form of iron, but is too impure and brittle to be used except for purposes where no great strength is required. It is purified and converted into wrought or malleable iron, and steel. Cast iron is *crystalline* in structure.

**Malleable, or wrought, iron.**—This variety is nearly pure iron, containing only from 0.12 to 0.25 per cent. of carbon, and melts at a higher temperature than cast iron. Malleable iron contains less than 0.5 per cent. of total impurities (carbon, sulphur, phosphorus, silicon). It is obtained from cast iron by the **puddling process**, invented by Cort in 1784. The cast iron is fused in a reverberatory furnace (Fig. 363), the hearth of which is lined with haematite, which oxidises the carbon:



the carbon monoxide bubbling through the molten iron. Sulphur, phosphorus, and silicon are oxidised and pass into the

slag. When the metal becomes pasty it is formed into lumps, or 'blooms,' which are beaten under steam hammers to squeeze out the slag. The iron, although not fused, *welds* together to a coherent mass below  $1000^{\circ}$ . Malleable iron is tough and *fibrous* in structure; its property of welding is exceedingly valuable and is applied in various ways by the blacksmith. Its softness is not appreciably altered by heating to redness and quenching in water, whereas steel then becomes very hard; wrought iron cannot be hardened or tempered as steel can. **Mild steel** is really malleable iron produced by the Bessemer or open-hearth processes to which a little carbon has been added to increase its strength, and its use is largely replacing that of wrought iron, although the latter is tougher than steel.

Iron containing combined phosphorus is brittle at the ordinary temperature and is said to be 'cold-short'; combined sulphur (probably as ferrous sulphide) makes it brittle when red-hot, or 'red-short.'

Pure iron, which occurs in the soft iron wire used for binding flowers, is too soft for general use. It is an almost white metal with a high melting point ( $1533^{\circ}$ ) and a fairly high specific gravity (7.9). Iron powder, prepared by the reduction of the oxide at fairly low temperatures by hydrogen, catches fire spontaneously in air, or is *pyrophoric*. Pure iron is also obtained by electrolysis of ferrous sulphate or ferrous chloride solutions, although other salts (e.g., calcium chloride or ammonium sulphate) may be added. As obtained it is brittle and charged with hydrogen, but on heating, the hydrogen is evolved and a very soft pure iron remains. Electrolytic iron tubes are made, and the deposits are also used for facing electrotypes.

Very pure iron, containing less than 0.1 per cent. of total impurity, called **Armco iron**, is made by a modification of the open-hearth process (p. 633).

**Steel.**—Steel is iron which has been fused in the process of manufacture and contains from 0.15 to 1.5 per cent. of carbon and generally a little silicon. It may also contain manganese, titanium, chromium, nickel, tungsten, and vanadium, which are purposely added to produce what are called **alloy steels**, used for special purposes. Steel is made (1) from cast iron by removing part of the carbon; (2) from malleable iron by adding carbon.

The best steel is made by adding carbon to wrought iron in



the **cementation process**. Bars of wrought iron are heated in fireclay boxes with charcoal for one or two weeks. Absorption of carbon gradually occurs, the carbonisation spreading slowly through the mass, and converting the iron into steel. The surface of the bars is covered with blisters, and the 'blister steel' is fused in plumbago crucibles to form cast steel or crucible steel. This is an expensive variety of steel and is made only in small quantities for razors and good cutlery.

Modern steel is produced by removing part of the carbon of cast iron by :

(1) **The Bessemer process.**

(2) **The open-hearth process or Siemens-Martin process.**

**The Bessemer process.**—This process is still largely used in Germany and America but has mostly been replaced in England

by the open-hearth process, which is said to produce a better steel. The molten pig iron from the blast furnace is run directly into a **converter** (Fig. 369), a large pear-shaped iron vessel, lined with refractory bricks. The converter is supported on trunnions, air being led by a pipe to a hollow perforated bottom, from which it is forced through the metal. The molten cast iron is added through the open mouth with the converter horizontal, and blowing is then begun. The

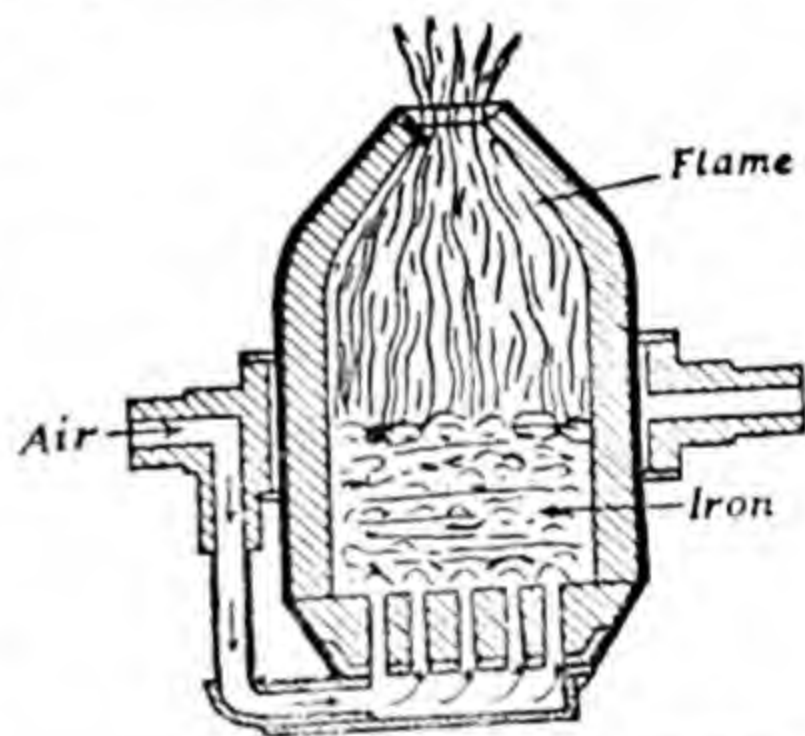


FIG. 368.—SECTION OF BESSEMER CONVERTER.

converter is next swung into a vertical position, and blowing continued. Silicon is first oxidised to silica which passes into the slag, then a portion of the iron is oxidised. The resulting ferric oxide removes the carbon, forming carbon monoxide, which is freely evolved and burns at the mouth of the converter as an orange-yellow flame edged with blue, shot through by showers of sparks. After six to eight minutes the flame sinks, indicating that the carbon has been removed. The purified iron is still liquid, owing to the very high temperature. The converter is again tilted, the blast stopped, and the requisite amount of *spiegeleisen*, an iron-manganese alloy rich in carbon, is added. The molten steel is poured, by further tilting the converter, into ladles supported by travelling cranes, from

which it is run into moulds. According to the percentage of carbon added, various kinds of steel are produced: **tool steel** (0.9-1.5 per cent. carbon); **structural steel** (0.2-0.6 per cent. carbon); **mild steel** (0.2 per cent., or less, carbon).

When the ores of iron contain phosphorus, the resulting iron or steel, if made in the ordinary way, would be 'cold-short,' *i.e.*, brittle when cold. Such ores are worked by the process of Thomas and Gilchrist, in which the usual silica ('acidic')



FIG. 360.—OPERATION OF THE BESSEMER CONVERTER.  
(By courtesy of 'The Scientific American'.)

lining of the converter is replaced by a 'basic' lining of magnesia and lime, prepared by calcining dolomite. Limestone or lime is first charged into the converter, along with coke, and the blast turned on. Molten pig iron is then run in and the blast continued. Carbon is first burnt out as usual, but if the blast is prolonged after the flame drops, the phosphorus is oxidised, unites with the lime added—*not* from the converter lining—and forms a slag containing basic calcium phosphate and free lime ('basic slag'), which is used as a fertiliser. **Spiegeleisen** is then added to form the steel.



The steel billets, produced in any process by casting, are *annealed* in underground furnaces ('soaking-pits') heated by blast-furnace gas, and are then passed through the rolling mills for the production of steel bars and sheets.

**\*The open-hearth process.**—The open-hearth process is carried out in a large flat crucible enclosed in a furnace (Fig. 370) heated by producer gas. The air and gas are supplied through separate heat regenerators of chequer brickwork, used in pairs and alternately traversed by the hot products of combustion and the gases, as in the Cowper stoves. The hearth is lined with ganister (silica rock) in the acid process or calcined magnesite or dolomite

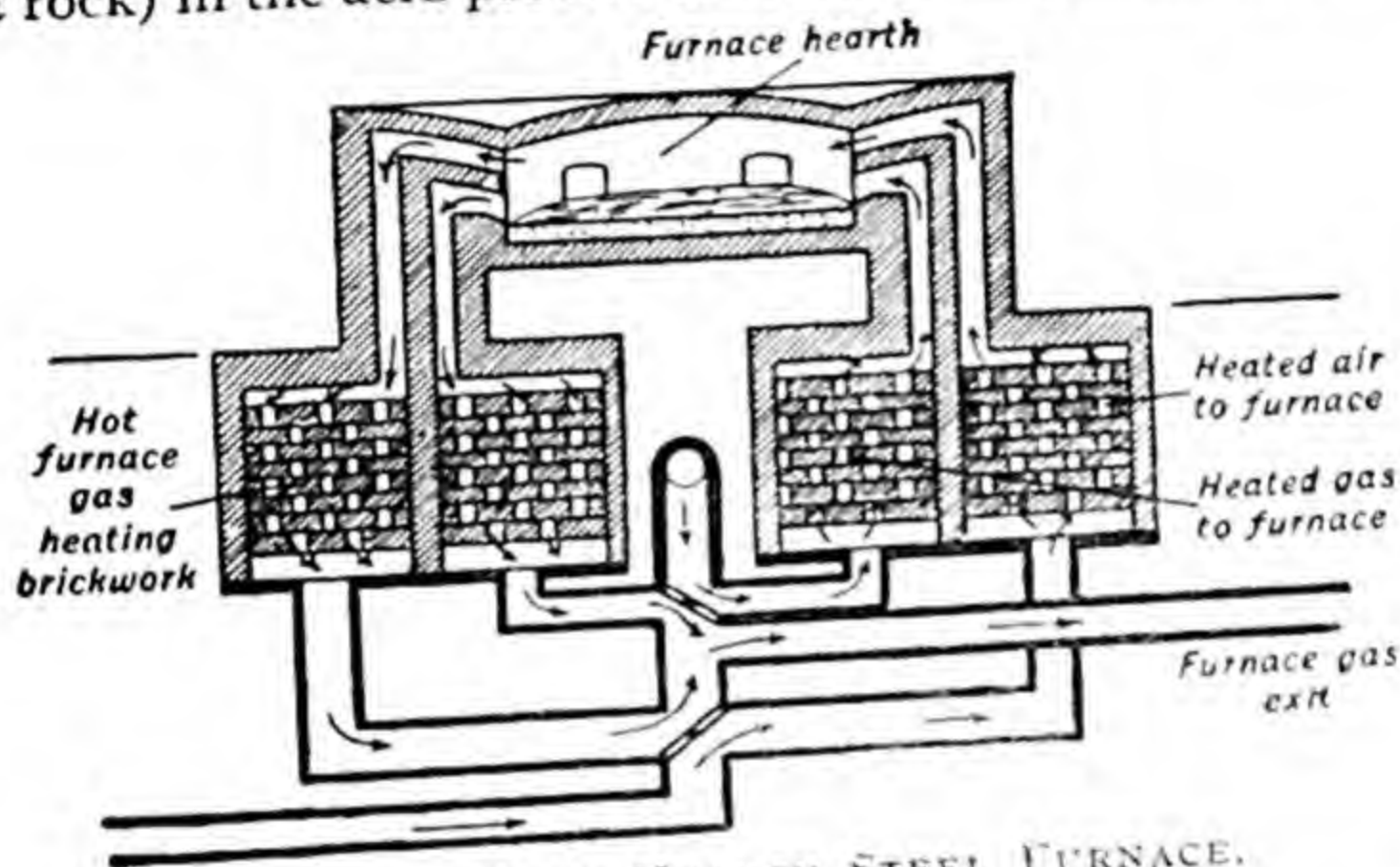


FIG. 370.—OPEN-HEARTH STEEL FURNACE.

in the basic process. The process is generally carried out with a mixture of pig iron and steel scrap, with limestone or lime in the basic process, together with some fluorspar as a flux. The molten charge evolves carbon monoxide, and the carbon and silicon are decreased by oxidation to the required amount, the phosphorus and sulphur being eliminated in the slag as in the basic Bessemer process. The furnace may be made to tilt and discharge a portion of its contents into the ladle. The operation lasts 8-10 hours; it produces a larger batch of steel at a time, is more easily controlled than the Bessemer process, and is now more largely used than the latter.

**Electric furnaces** are used in the production of special high quality steels. They are mostly on the arc principle, and consist of refractory crucibles containing two (or more) large vertical carbon electrodes between which an electric arc is struck.

The temperature is very high and the difficultly fusible alloy steels may be produced in such furnaces.

**\*The properties of steel.**—The properties of steel depend on the content of carbon : low-carbon steels are soft, like wrought iron, and are known as mild steel ; with further addition of carbon the ductility falls, whilst the tensile strength increases up to a limiting percentage of carbon. Wrought iron and mild steel are malleable and may be welded. The melting point of steel is lower than that of wrought iron. The properties of steel depend

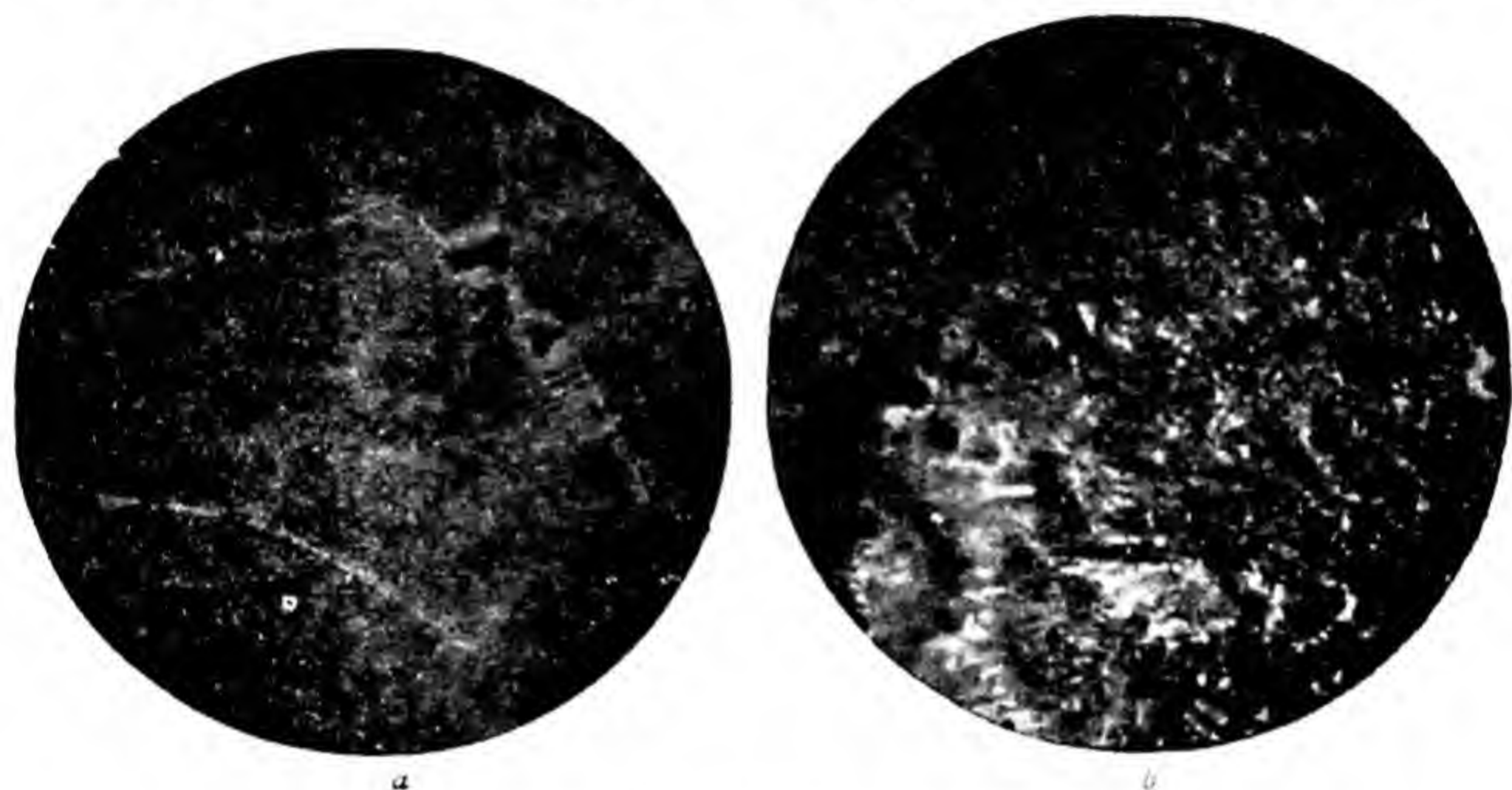


FIG. 371.—PHOTOMICROGRAPHS OF :

(a) PURE ANNEALED IRON, SHOWING LARGE CRYSTALS ALMOST ENTIRELY FREE FROM INTERCRYSTALLINE MATERIAL; THE METAL IS VERY SOFT; (b) HARD STEEL, AN AGGREGATE OF SMALL CRYSTALS CONTAINING CARBON IN SOLID SOLUTION IN IRON.

also on the *heat treatment* to which the metal has been subjected. If steel is heated to redness and plunged into cold water, it becomes as hard and brittle as glass. If it is now heated to various temperatures, the resulting metal possesses properties depending on the temperature. This operation is known as **tempering**, and the temperature may be judged by the colour of the thin film of oxide produced on a bright surface of the metal :

- 230° : light straw colour : used for razor blades.
- 255° : brownish-yellow : used for penknives and axes.
- 277° : purple : used for cutlery.
- 288° : bright blue : used for watch-springs and swords.
- 290°-310° : dark blue : used for chisels and large saws.



The changes taking place in the annealing of steel are rather complicated. There are three allotropic forms of iron: (1)  $\alpha$ -iron, stable below  $900^{\circ}$ , soft and magnetic, and capable of dissolving only very little carbon; (2)  $\gamma$ -iron, formed from  $\alpha$ -iron at the transition point  $900^{\circ}$  (*cf.* p. 346), non-magnetic and capable of dissolving carbon to form a solid solution; (3)  $\delta$ -iron, formed from  $\gamma$ -iron at  $1400^{\circ}$ . The  $\alpha$ -iron becomes non-magnetic about  $760^{\circ}$ , but this is not an allotropic change into a  $\beta$ -iron, as was formerly thought, but a physical change.

The crystal lattice (see p. 190) of all three forms of iron is cubic, but whereas  $\alpha$ -iron and  $\delta$ -iron have a *body-centred lattice* (with an iron atom at the centre of each unit cube),  $\gamma$ -iron has a

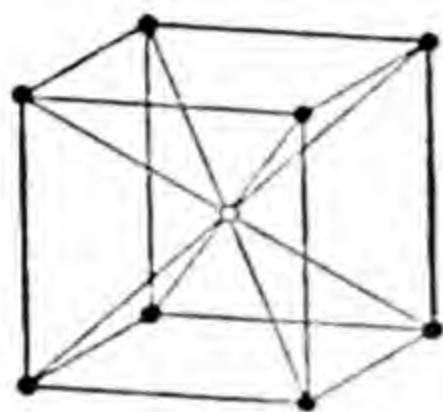


FIG. 372.—BODY-CENTRED CUBIC LATTICE.

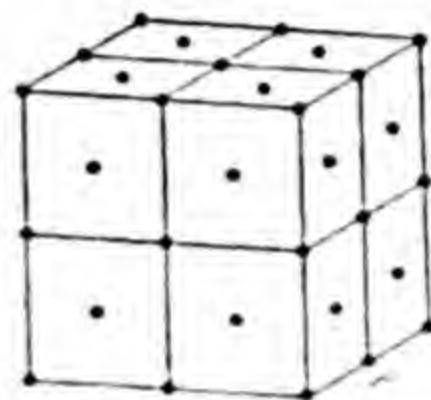


FIG. 373.—FACE-CENTRED CUBIC LATTICE.

*face-centred lattice* (with an iron atom at the centre of each face of the cube and shared by two cubes). These are shown in Figs. 372 and 373 respectively.

The unit cubes have iron atoms at the corners as well as at the centres or faces, and are extremely small, there being over 10 million in a *length* of 1 inch. When  $\alpha$ -iron changes to  $\gamma$ -iron the length of the cube side increases, but as there are more iron atoms in the  $\gamma$ -iron cube the net result is actually a contraction.

When solid steel containing carbon is *slowly cooled*, the carbon remains dissolved in the  $\gamma$ -iron above  $900^{\circ}$ . Below this temperature  $\alpha$ -iron forms and, as this does not dissolve carbon, the carbon separates as hard grains of cementite (iron carbide,  $\text{Fe}_3\text{C}$ ) in a soft matrix of  $\alpha$ -iron. By *rapid cooling*, however, the carbon remains dissolved as a kind of supersaturated solution, forming a hard brittle steel, with needle-shaped crystals, called **martensite**. In annealing, some carbon separates as hard grains of cementite, and the iron matrix is softened.

Wrought iron is **case-hardened** by heating in contact with carbon or potassium ferrocyanide, when a surface layer of steel is produced, giving a very hard surface of high-carbon steel (which would be too brittle if used alone) with a very tough body of mild steel (which itself would be too soft). **Armour plate** is made by case-hardening a sheet of soft steel on one side and then spraying it with cold water. It is pierced in a clean hole by a soft-nosed shell, whereas hard steel splits in pieces. Nickel-chrome steels form very tough armour plates.

Steel is difficult to cast free from flaws, whilst cast iron has not usually sufficient strength. If the cast iron is cast in a metal mould so as to cause rapid chilling, the cementite may be removed by heating the casting embedded in haematite for several days. The combined carbon on the surface is oxidised and that from the interior diffuses out to replace it. Finally the carbon content is reduced to that of steel and the metal is cooled. This is a **malleable casting**. In America the cementite in the interior is caused to decompose with separation of *fine* graphite and the iron becomes soft: the result is called a 'black-heart casting,' since it is white outside with a black core.

**\*Special alloy steels.**—In recent years great progress has been made in the production of steels containing what were formerly often 'rare' metals; these steels, *after suitable heat treatment*, possess valuable properties, and in advertisements of motor cars, for example, the axles are often described as composed of vanadium steel, the valves of nickel steel, etc.

**Manganese steel**, containing 9-14 per cent. manganese, is very tough and wear-resisting, and is used for rails exposed to heavy wear (on bends in the track), for the jaws of rock-crushers, safes, etc. Sir Robert Hadfield, of Sheffield, was one of the pioneers of modern steels with his invention of manganese steel in 1888. It is used directly as quenched and cannot be annealed.

**Nickel steel** has a higher tensile strength than common steel; nickel-chromium steel containing 3 per cent. of nickel, 0.5 to 1.5 per cent. of chromium and 0.3 per cent. of carbon is a useful kind and is applied in making cables, propeller shafts, and aeroplane, motor-car and bicycle parts. It does not require quenching but can be hardened by cooling in air. When it contains a larger proportion of nickel it resists corrosion, and is used in motor engines for the exhaust valves, which are exposed to the very hot gases passing out after the explosion in the cylinder. Steel containing 36 per cent. of nickel is called *invar*, and scarcely expands on heating.



*Chromium-vanadium steel* (1 per cent. chromium, 0.15 per cent. vanadium) is very tough but ductile and can be bent double when cold without breaking: it is used for motor car frames and front axles. *Tungsten steel* is used for permanent magnets; *silicon steel* for electromagnets; *cobalt steel* retains permanent magnetism in a remarkable degree, and is used in permanent magnets of magnetos; *chromium-tungsten* or *chromium-molybdenum steels*, heated to  $1300^{\circ}$  and quenched, remain hard even when red hot and are used for 'high speed' lathe chisels and engine valves. They generally also contain some vanadium. *Stainless steel* is an alloy of ordinary steel (0.3 per cent. of carbon) with 12-14 per cent. of chromium and a little nickel. The 'flints' of automatic lighters are made of an alloy of steel with a rare-earth metal, *cerium* (a residue from gas mantle manufacture, *q.v.*) and give off showers of sparks when abraded by a carborundum wheel.

**The rusting of iron.**—The one great drawback to the use of iron is that the metal when exposed to ordinary moist air is quickly corroded to a reddish-brown rust, consisting chiefly of hydrated ferric oxide. The conditions under which rusting takes place have been investigated by several experimenters, with divergent results. The homogeneity or otherwise of the metal and its purity affect the results. The presence of water is essential, and according to some experimenters the presence of carbon dioxide is also necessary. Freshly-formed rust usually contains considerable quantities of ferrous hydroxide and carbonate, indicating that the formation of these compounds is probably the first step in the corrosion of the metal:

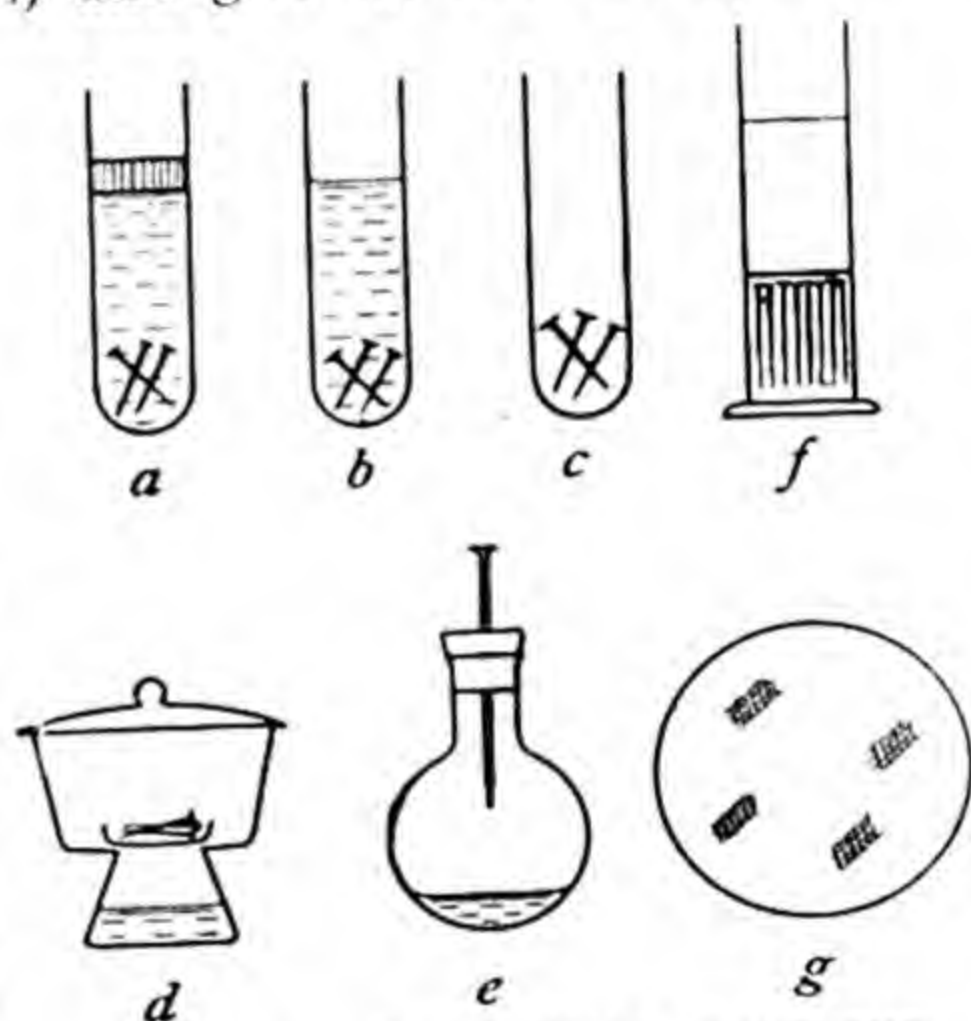
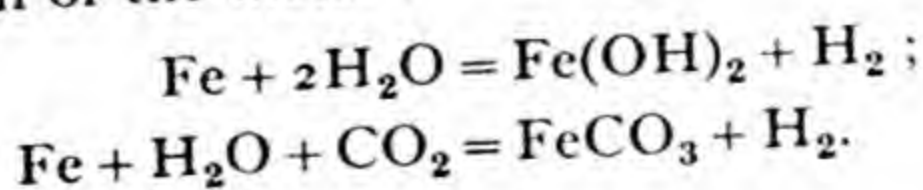


FIG. 374.—EXPERIMENTS ON THE RUSTING OF IRON.

The following simple experiments throw some light on the rusting of iron. Four lots of clean iron nails are taken.

(a) Ordinary tap water is boiled in a test-tube until it begins to bump, showing that dissolved air has been expelled. The first lot of nails are put in and the boiling continued for half a minute, when melted vaseline is poured on the top of the water to exclude air. Here iron + water are present, and *the iron does not rust* on standing.

(b) The second lot of nails are put into a test-tube filled with tap water. Here iron + oxygen + much water + carbon dioxide are present, and *the iron rusts* on standing.

(c) The third lot of nails are put into a test-tube with a little water, and the iron again rusts on standing, the conditions being similar to those in (b) except that less water is present.

(d) The fourth lot of nails are put into a desiccator over concentrated sulphuric acid. Here iron + air alone are present and *the iron does not rust*.

(e) The following experiment shows that carbon dioxide is required to produce rust. About 100 c.c. of 15 per cent. caustic potash solution is poured into a 500 c.c. flask fitted with a partly bored cork. The solution is shaken in the flask and after standing for two days all the carbon dioxide will have been abstracted from the air in the flask. A large bright nail is boiled with distilled water as in Expt. (a) and then pushed through the cork of the flask, a short length being left outside. The part of the nail outside rusts as usual, but the part inside, exposed to air + water vapour, but no carbon dioxide, *does not rust*.

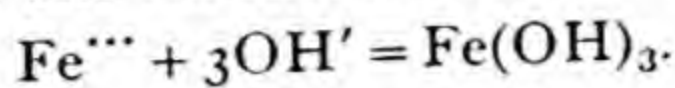
(f) The under parts of the nails in Expt. (b) remain bright, rust being deposited on the tops, nearest the air. This indicates that iron may pass into solution, which is then oxidised by exposure to air. If nails packed vertically in a jar are covered with a piece of hardened filter paper, and the whole covered with boiled distilled water, it will be found that rust is deposited *above* the filter paper on standing.

According to another theory of rusting, the different parts of a piece of iron act as poles of voltaic cells and solution of the metal occurs as the result of local action. This is quite compatible with the fact that oxidation occurs only in solution, since ferrous ions may be formed initially by the action of hydrogen ions from water or carbonic acid:  $\text{Fe} + 2\text{H}^+ = \text{Fe}^{++} + 2\text{H} = \text{Fe}^{++} + \text{H}_2$ .

In presence of air the dissolved ferrous iron is oxidised to ferric iron:  $4\text{Fe}^{++} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Fe}^{+++} + 4\text{OH}'$ .



The ferric ions and hydroxide ions then precipitate as ferric hydroxide, which is one constituent of rust (see above) :



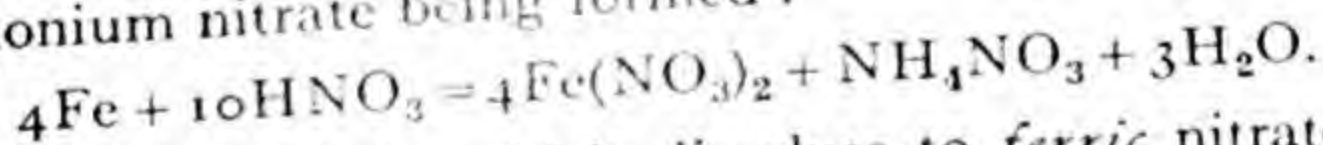
The following experiment illustrates the voltaic theory :

(g) A solution of agar-agar in hot water ( $1\frac{1}{2}$  per cent.), to which is added a little sodium chloride and phenolphthalein, is poured over a clean plate of iron in a glass dish. The agar sets to a jelly. After some hours red patches appear, indicating the formation of caustic soda by electrolysis. If potassium ferricyanide and phenolphthalein are added to the agar, the anodes become blue, from reaction of ferricyanide with ferrous ions, and the cathodes red, from the caustic potash formed.

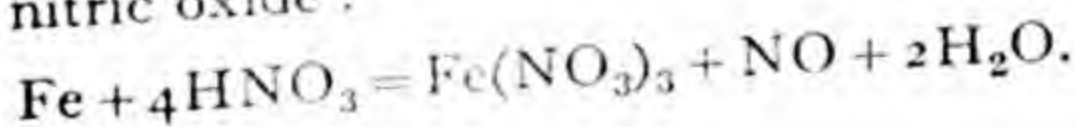
Iron is protected from rusting by painting, or whitewashing with lime. Pipes are also protected by heating and dipping into a solution of coal-tar pitch in coal-tar naphtha, when an impervious coating is formed (*Angus Smith's compound*). In the *Barff process*, the iron is heated to redness and steam blown over it, when an adherent layer of ferroso-ferric oxide is formed. This is used in treating cans for fruit, etc., instead of tinning. The layer of oxide is removed by heating with water containing magnesium chloride, which explains the corrosive action of sea water on boilers.

**\*Passive iron.**—Iron is rendered *passive* by immersion in *cold concentrated* nitric acid. The metal is then insoluble in dilute acids, and does not precipitate copper from a solution of copper sulphate. The passivity is removed by touching with active iron under the surface of dilute sulphuric acid. The passivity is due to a transparent film of oxide.

Iron dissolves slowly in *cold dilute* nitric acid, *ferrous* nitrate and ammonium nitrate being formed :



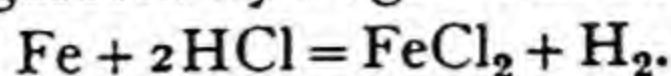
In *warm dilute* nitric acid it dissolves to *ferric* nitrate with evolution of nitric oxide :



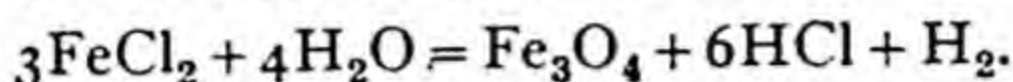
#### FERROUS SALTS, $\text{FeX}_2$

**Ferrous chloride.**—This salt,  $\text{FeCl}_2$ , is deposited from solutions of iron in hydrochloric acid in bluish-green crystals,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , which oxidise slightly, and become green, in the air. The

anhydrous chloride,  $\text{FeCl}_2$ , is obtained in white lustrous scales on heating iron in gaseous hydrogen chloride :



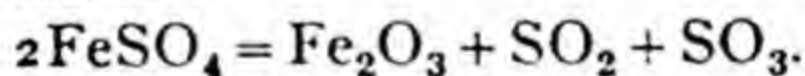
Anhydrous ferrous chloride volatilises at a bright red heat ; its vapour density indicates that molecules of  $\text{Fe}_2\text{Cl}_4$  and  $\text{FeCl}_2$  are present. When ferrous chloride is heated in steam, hydrogen is evolved :



**Ferrous sulphate.**—This is the most important ferrous salt,  $\text{FeSO}_4$ , and is obtained by dissolving iron in dilute sulphuric acid, or by the slow oxidation of *marcasite*, or 'coal-brasses,'  $\text{FeS}_2$ , by air in presence of water. The common form is *green vitriol*, or *copperas*,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , in light-green crystals.

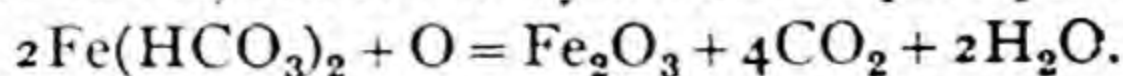
Ferrous sulphate readily forms double salts with the sulphates of the alkali metals,  $\text{R}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ . If equimolecular amounts of ferrous sulphate and ammonium sulphate are dissolved in separate amounts of warm water, and the filtered solutions mixed, **ferrous ammonium sulphate**  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ , is deposited on cooling in light bluish-green crystals, much less readily oxidised by atmospheric oxygen than ferrous sulphate ; it contains almost exactly one-seventh of its weight of ferrous iron.

When the green crystals of ferrous sulphate hydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , are heated they first of all lose water and form a white amorphous mass of the anhydrous salt,  $\text{FeSO}_4$ . When this is more strongly heated, it decomposes, with evolution of sulphur dioxide and sulphur trioxide (which forms dense white fumes of sulphuric acid in moist air) and a red powder, consisting of ferric oxide, remains :



This reaction was formerly used in the preparation of sulphuric acid. (Copper sulphate is scarcely decomposed at a red heat.)

**Ferrous carbonate.**—This compound,  $\text{FeCO}_3$ , occurs as *siderite*, or *spathic iron ore*, isomorphous with calcite. It is formed as a white precipitate on addition of an alkali carbonate to ferrous salts. The precipitate rapidly becomes green, and finally brown, on exposure to air, owing to oxidation to ferric hydroxide. The addition of sugar retards the oxidation. Ferrous carbonate dissolves in water containing carbonic acid, forming **ferrous bicarbonate**,  $\text{Fe}(\text{HCO}_3)_2$ , which is sometimes present in rivers. On exposure to air, red ferric hydroxide is precipitated :

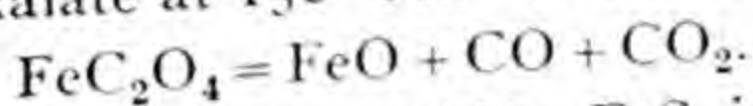


Plants absorb iron from the soil as the bicarbonate.

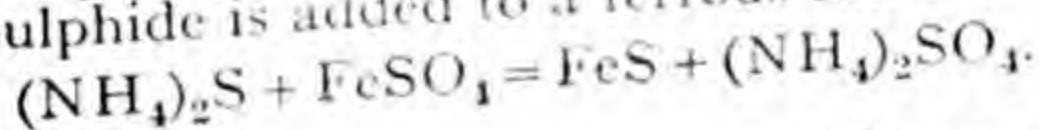


**Ferrous hydroxide.**—This compound,  $\text{Fe}(\text{OH})_2$ , is thrown down as a white precipitate when caustic soda is added to a pure solution of a ferrous salt, with absolute exclusion of air. It is insoluble in excess of alkali. The precipitate rapidly becomes green in the air, from formation of hydrated  $\text{Fe}_3\text{O}_4$ , and finally brown, forming  $\text{Fe}(\text{OH})_3$ .

**Ferrous oxide**,  $\text{FeO}$ , is formed as a pyrophoric black powder by reducing ferric oxide with hydrogen at  $300^\circ$ , or by adding ferrous oxalate (obtained by precipitating ferrous sulphate with ammonium oxalate) to boiling caustic potash. A mixture of  $\text{FeO}$  and finely-divided iron, which is pyrophoric, is obtained by heating ferrous oxalate at  $150^\circ$ - $160^\circ$  in absence of air :



**Ferrous sulphide.**—Ferrous sulphide,  $\text{FeS}$ , is formed as a black mass by heating iron filings together with sulphur, a considerable amount of heat being evolved. A mixture of iron filings and sulphur when moistened becomes heated and forms  $\text{FeS}$ . Ferrous sulphide when pure is a yellowish, crystalline mass with a metallic lustre. The commercial substance is black or dark-grey, and contains free iron. It dissolves readily in dilute acids, and is used in the preparation of sulphuretted hydrogen. A greenish-black precipitate of ferrous sulphide is formed when ammonium sulphide is added to a ferrous salt :

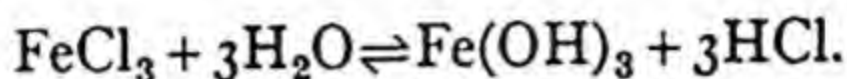


**Iron disulphide**,  $\text{FeS}_2$ , occurs native in two forms as *iron pyrites* and *marcasite*, and can be obtained by gently heating ferrous sulphide with sulphur. *Pyrites* is stable in air, *marcasite* oxidises in moist air to ferrous sulphate and crumbles down to a powder.

#### FERRIC SALTS, $\text{FeX}_3$

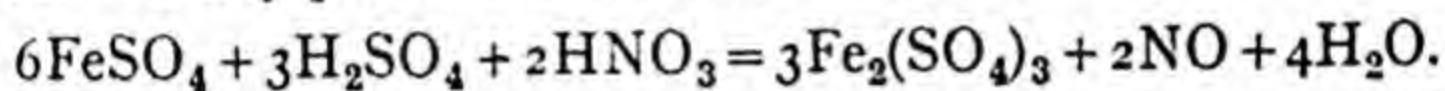
**Ferric chloride.**—This, the most important ferric salt,  $\text{FeCl}_3$ , is obtained anhydrous, in iron-black crystals with a green iridescence, on heating iron in chlorine. These volatilise on heating, and at  $444^\circ$  the vapour density corresponds with  $\text{Fe}_2\text{Cl}_6$ . With rise of temperature the vapour density falls, owing to dissociation into  $\text{FeCl}_3$  molecules. The anhydrous chloride is soluble in benzene forming a bright yellow solution, the colour being due to the unionised  $\text{FeCl}_3$  molecules. The same colour is shown by an aqueous solution in presence of excess of hydrochloric acid, which represses ionisation. The ferric ion,  $\text{Fe}^{+++}$ , is probably colourless.

Aqueous solutions of ferric chloride are produced by dissolving ferric hydroxide in hydrochloric acid, or by saturating solutions of ferrous chloride with chlorine. On evaporation, yellow crystals of the hydrated chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , are deposited on cooling, readily soluble in water. Ferric chloride solution is used as a styptic, *i.e.* in stopping bleeding. It coagulates the blood, forming a clot. The solution is strongly acid, due to hydrolysis :

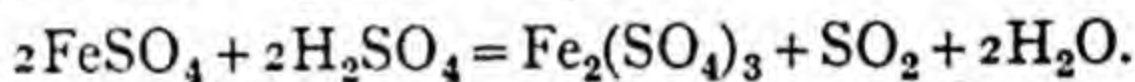


On heating the hydrated salts, hydrochloric acid is evolved, and a basic salt, or finally ferric oxide, is left.

**Ferric sulphate.**—A solution of this salt,  $\text{Fe}_2(\text{SO}_4)_3$ , is obtained by boiling ferrous sulphate with dilute sulphuric and nitric acids. Nearly pure nitric oxide is evolved :

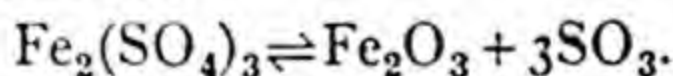


Ferric sulphate is also formed by evaporating ferrous sulphate with concentrated sulphuric acid :



Anhydrous ferric sulphate is a yellowish-white powder, dissolving only very slowly in water, but ultimately forming a very concentrated solution. This is brown-red owing to hydrolysis, but becomes paler on addition of sulphuric acid. The salt crystallises from solution with seven molecules of water of crystallisation. With potassium and ammonium sulphates ferric sulphate forms iron alums, *e.g.*,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , with a violet colour when pure, but often pale yellow, owing to the presence of ferric oxide. These are readily soluble in water, and are not appreciably hydrolysed. The potassium alum,  $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , does not crystallise so readily as the ammonium salt.

On heating ferric sulphate, sulphur trioxide is evolved, the reaction being reversible :



Ferric sulphide,  $\text{Fe}_2\text{S}_3$ , is obtained by the action of hydrogen sulphide on moist ferric hydroxide, as in the process for the removal of hydrogen sulphide from coal gas (p. 344), but it is not very stable.

**Ferric hydroxide.**—If ammonia is added to a solution of a ferric salt, a reddish-brown, gelatinous precipitate, generally called ferric hydroxide, is thrown down, which is slimy in the cold



but becomes flocculent on boiling. It is practically insoluble in water and alkalies. The precipitate is colloidal, and dries to a gum-like mass of indefinite composition. Crystalline hydrated ferric oxide of the composition  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is known. On ignition of the hydrated oxides, brownish-red ferric oxide,  $\text{Fe}_2\text{O}_3$ , is formed, which in this state is nearly insoluble in acids. Red varieties of ferric oxide are formed by igniting ferrous sulphate in the air, and are used as paints or as a polishing powder (*rouge, crocus, colcothar*).

When ferric oxide is fused with potassium nitrate a purple soluble potassium ferrate,  $\text{K}_2\text{FeO}_4$ , is formed.

Colloidal ferric hydroxide is obtained by dissolving freshly-precipitated ferric hydroxide in a concentrated solution of ferric chloride, and dialysing. The blood-red solution is called *dialysed iron*.

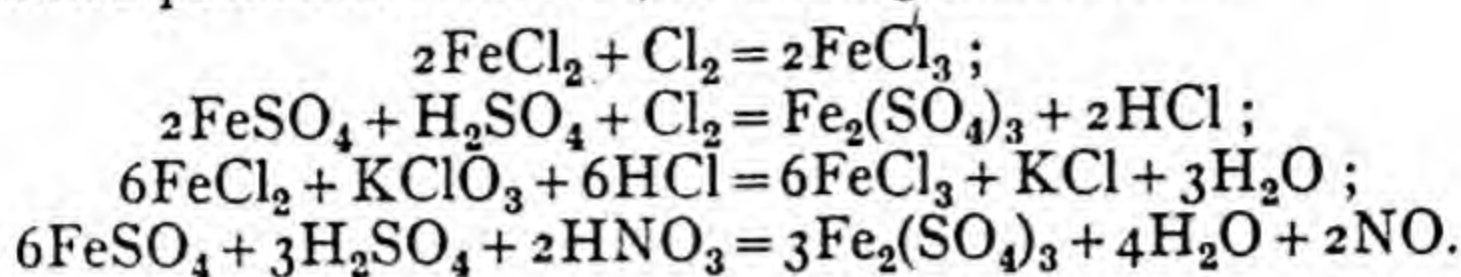
It must be noted that ferric oxide is *not* obtained by heating iron in air, oxygen, or steam, although the hydrated form is produced by the slow rusting of iron. The product in the first case is a compound of ferrous and ferric oxides,  $\text{Fe}_3\text{O}_4$ , *ferroso-ferric oxide*, which is strongly magnetic ('smithy scales'). It is melted and cast into electrodes, since it resists acids and chlorine when fused. Hydrated ferroso-ferric oxide is formed as a black precipitate by adding sodium hydroxide to a mixture of a ferrous and a ferric salt in solution. It is more easily filtered than ferric hydroxide (see p. 334).

**Tests for iron.**—Iron in solution is detected by the following reactions:

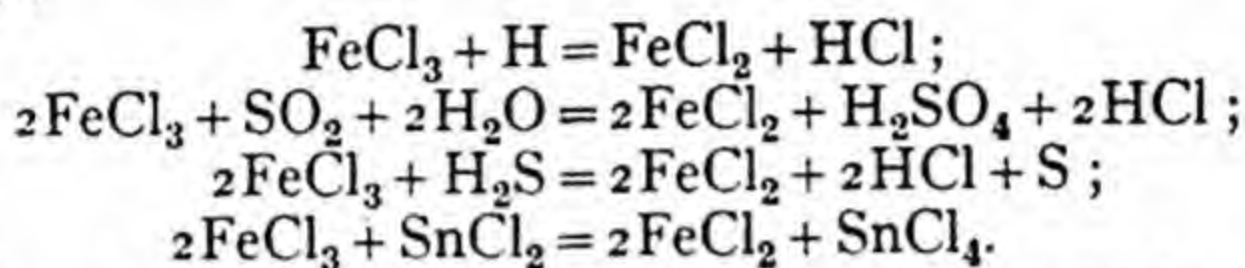
REAGENT	FERROUS IRON	FERRIC IRON
Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$	white or pale blue pp.	deep blue pp. (Prussian blue)
Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$	deep blue pp.	no pp. but dark brown colour
Potassium thiocyanate KCNS	no colour	deep blood red colour,

Many soluble ferrous salts are green, and ferric salts yellow or brown. It may be noted, however, that *ferrous oxalate*,  $\text{FeC}_2\text{O}_4$ , is yellow, whilst *ferric oxalate*,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ , is green.

Ferrous salts are *oxidised* to ferric salts by chlorine, bromine, acidified potassium chlorate, or boiling nitric acid :



Ferric salts are *reduced* to ferrous salts by nascent hydrogen (*e.g.*, zinc and dilute sulphuric acid), by sulphur dioxide, by hydrogen sulphide (with deposition of sulphur), and by stannous chloride :



**\*Cobalt.**—Cobalt and nickel are two metals which resemble iron in many ways and occur in the same group in the periodic system (p. 236). Cobalt, which is mostly extracted from ores in Ontario, has so far not found such extensive application as nickel, but it is used alloyed with iron, as *cobalt steel* (35 per cent. cobalt) in making permanent magnets for magnetos. These magnets can be made much smaller than carbon steel magnets and they retain their magnetism much more tenaciously, and so do not tend to become demagnetised. *Stellite* (p. 566) is a useful cobalt alloy ; an alloy of cobalt, iron, and chromium, called *Festel metal*, is used for cutlery.

Cobalt compounds are used in making blue glass (p. 595) and blue enamels. When fused with silica and alkali (potash) they give an intensely deep blue mass (*smalt*), used as a pigment. Cobalt plating has also been attempted : the metal is said to adhere well to steel and shows no tendency to strip at the edges. *Thenard's blue* is a pigment obtained by heating freshly precipitated cobalt phosphate with freshly precipitated alumina ; *Rinman's green* is a pigment obtained by heating cobalt phosphate with zinc hydroxide. Cobalt compounds have also been used as 'driers' for paints.

**\*Nickel.**—This metal is extensively used for **nickel plating**, a process in which the metal is deposited electrolytically from a solution of a nickel salt. Finely divided nickel is also used as a catalyst in hardening oils (p. 292). Alloys of iron and nickel (*nickel steel*) have valuable properties. An interesting technical process for the extraction of nickel, the *Mond process*, depends on the formation of a volatile compound of nickel and carbon



monoxide, **nickel carbonyl**,  $\text{Ni}(\text{CO})_4$ , when carbon monoxide is passed over the ore in which the nickel has been reduced to the metallic state. The metal is carried away in the gaseous form in the form of the carbonyl, and this is decomposed by heat into carbon monoxide and metallic nickel.

It is generally said that 'nickel is remarkably stable towards atmospheric oxidation,' but in town air it is rapidly covered with a green patina. Chromium plating, which is permanently bright, has replaced nickel plating, although it must be applied to an undercoat of nickel plating. The chromium is probably covered with an invisible film of oxide.

In nickel plating iron, steel, or brass, layers of nickel varying from 0.0002 of an inch down to as little as 0.00005 of an inch are used, but these deposits are somewhat porous, and the iron readily rusts through any small opening in the nickel coating, the latter then peeling off. By using a 0.001 inch deposit it is possible to obtain a product which will be stable in appearance and free from rust over a reasonable period of time.

Malleable nickel is used in the dairy for the construction of various types of milk handling and treating machinery, such as pasteurisers and milk cans, replacing principally tinned copper: it is very little affected by milk products and does not impart any perceptible taste to them.

A group of alloys consisting chiefly of nickel, chromium and iron are called **heat resistant**, or **electrical alloys**, because they do not oxidise or scale readily at high temperatures. They have good mechanical properties and strength at these temperatures, and have high electrical resistance and low temperature coefficients. In recent years probably 1,200 tons of nickel are used annually in the production of these alloys. They are now used for large cylindrical retorts for chemical operations at temperatures as high as  $1200^\circ \text{C}$ ., to a considerable extent in furnace construction, in conveying equipment for continuous heating or annealing furnaces, and for baffle plates, floor supports, bolts, chains, and screw shafts. There is a considerable use for them in equipment for the rolling and handling of glass.

One of the recent developments in automobile construction is the increased use of 5 per cent. nickel steel for case-hardened gears; its high strength and resistance to impact and its superior resistance to wear (probably due partly to its high hardness, but more particularly to its high fatigue resistance), make it very suitable for this rather exacting purpose.

Alloys containing about 78 per cent. nickel, and the rest

iron, known as *Permalloy*, *Mumetal*, etc., and distinguished by remarkable magnetic permeability at low magnetic intensities, have recently been used in telephone, cable, and radio-communication. For some time the manufacturers of electric light bulbs have used a copper-sheathed alloy of iron with about 38 per cent. nickel for the sealing-in wires passing through the glass.

Nickel is used also to some extent in light aluminium sand castings for hardening the alloy: an interesting alloy of this sort is the 'Y' alloy of the National Physical Laboratory, which contains: copper, 4; nickel, 2; magnesium, 1.5; aluminium, 92.5, and was developed originally for automobile pistons, which must have a high tensile strength at high temperatures. **Monel metal** is an alloy of nickel and copper obtained directly from the ore at Sudbury, Ontario. It has great tensile strength and is very resistant to oxidation and chemical corrosion, especially towards hot alkaline solutions. Monel metal is largely used for turbine blades especially when superheated steam is used. It is difficult to cast, forge, and machine.

Nickel copper alloys have been in use for a considerable time in China for coinage, and are also extensively used in America and on the Continent of Europe for the same purpose instead of bronze.

A Bactrian coin dated 235 B.C. consists mainly of an alloy of copper and nickel, produced by smelting a natural sulphide of copper and nickel. Such an alloy was known to the Chinese, who called it *paktong* (usually misread 'pakfong') or 'white copper.' After the discovery of nickel by Cronstedt in 1751, its presence in *paktong* was discovered, but it was not until about 1823 that the alloy was manufactured in Europe. Its use for coinage began in Switzerland in 1850. The modern *nickel silver* is an alloy of copper and nickel.



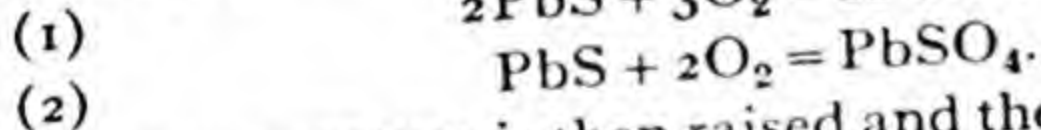
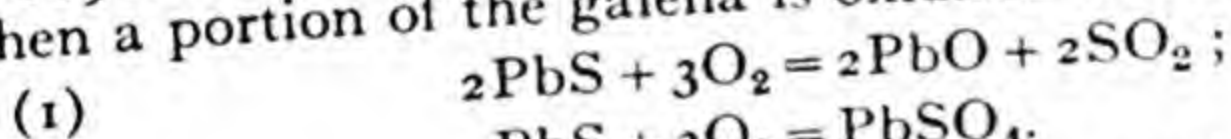
## CHAPTER XXXVI

### LEAD AND TIN

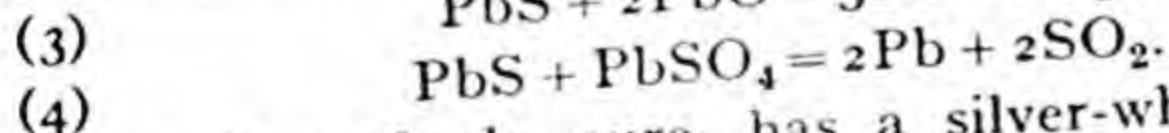
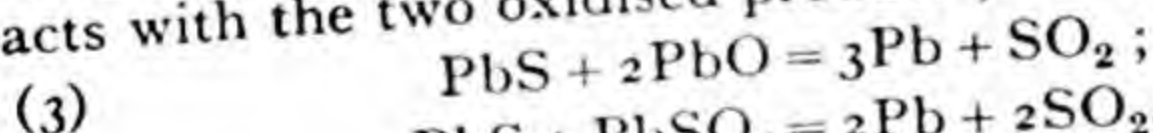
**Lead.**—The metal lead, which is easily reduced from its ores, was known in ancient Babylonia and Egypt; a small lead statue in the British Museum (Fig. 16) is attributed to the First Dynasty (3400 B.C.). Lead is mentioned in Job xix; it was at first confused with tin, but the difference was recognised by Pliny, who calls tin *white lead*.

Lead is widely distributed in the mineral kingdom; traces occur in the native form, but the chief ore is *galena*, the sulphide,  $\text{PbS}$ , which is a heavy mineral with a bright lustre.

Lead extraction was carried on in England during the Roman occupation (a considerable quantity of Roman lead remains at Bath), and smelting in Derbyshire was in active operation in the eighteenth century. The process is carried out largely in reverberatory furnaces (Fig. 363), known as **Flintshire furnaces**, in use in 1698. The ore is first roasted at a moderate temperature, when a portion of the galena is oxidised to oxide and sulphate:



The temperature is then raised and the remaining lead sulphide reacts with the two oxidised products, the metal being formed:



Lead, if perfectly pure, has a silver-white lustre, but has usually a bluish-grey colour. It is very soft, dense, and fusible. It is plastic, especially when heated, when it may be 'squirted' into wire or tubing by forcing it through a die under pressure, or 'wiped' in forming pipe-joints in plumbing. The so-called 'compo' tubing contains lead and a little antimony. Octahedral crystals of lead are obtained by fusing the metal and allowing to cool, or by precipitating it from a solution of the acetate or nitrate by zinc ('lead tree').

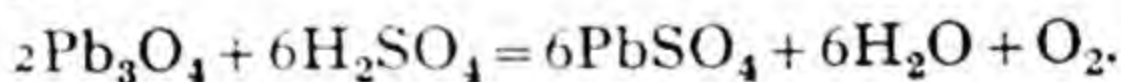
Lead oxidises rapidly but superficially in moist air, a white film of hydroxide and carbonate being deposited. **Pyrophoric lead**, obtained by heating the tartrate, ignites spontaneously in air (p. 282). The metal is not attacked by pure water (except at the boiling point), or by dry air, but is rapidly corroded in moist air or in soft water containing dissolved air and carbonic acid, forming a white deposit of lead hydroxide,  $\text{Pb}(\text{OH})_2$ , which is appreciably soluble in water, rendering the latter poisonous. Some lead carbonate is also formed. *Hard* water, containing calcium bicarbonate, has much less action on lead than soft water, and an adherent protective coating is formed on the metal.

Lead salts of the colourless bivalent ion,  $\text{Pb}^{++}$ , are powerful cumulative poisons, *i.e.*, small quantities below the poisonous dose accumulate in the system, and ultimately induce chronic poisoning. A characteristic symptom of **lead poisoning**, to which painters, plumbers, and potters using lead glazes are subject, is a blue line on the edges of the gums.

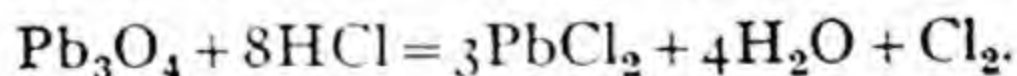
**Lead monoxide**,  $\text{PbO}$ , is formed as a yellow powder called *massicot* on heating lead in air. If fused, and powdered, the reddish-yellow crystalline form known as *litharge* is obtained. Litharge, obtained in the refining of silver, is largely used in making flint-glass, in glazing pottery, in preparing lead salts, and in making paints and varnishes. If litharge is boiled with water and olive oil, **lead oleate**, which is a sticky adhesive mass used in making lead plaster, is formed, and glycerin passes into solution.

**Red lead**, or **minium**,  $\text{Pb}_3\text{O}_4$ , formed by roasting massicot in air, is a scarlet crystalline powder. It decomposes again at higher temperatures:  $2\text{Pb}_3\text{O}_4 \rightleftharpoons 6\text{PbO} + \text{O}_2$ . Red lead is used in making flint glass.

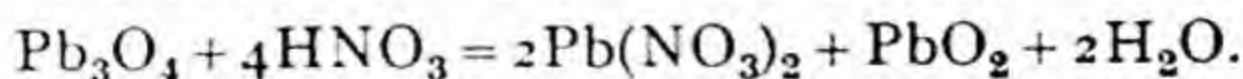
When heated with concentrated sulphuric acid, red lead evolves oxygen:



When warmed with concentrated hydrochloric acid it evolves chlorine:



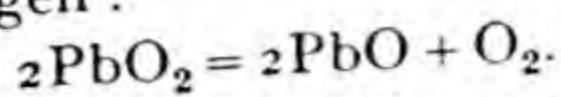
When red lead is treated with concentrated nitric acid, it is decomposed into lead nitrate and **lead dioxide** (or **lead peroxide**):



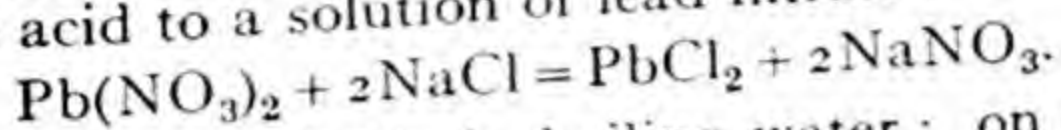
On washing out the nitrate with water, the dark chocolate-



brown dioxide remains. This oxide decomposes on heating into litharge and oxygen :



It oxidises many substances readily ; sulphur dioxide converts it into lead sulphate. With concentrated hydrochloric acid, an unstable yellow lead tetrachloride,  $\text{PbCl}_4$ , is first formed but easily decomposes with evolution of chlorine and formation of lead chloride,  $\text{PbCl}_2$  (*cf.*  $\text{MnO}_2$ , p. 313). A white precipitate of lead chloride is produced by adding a soluble chloride or hydrochloric acid to a solution of lead nitrate :



The precipitate is soluble in boiling water : on cooling, it is deposited in white needle-shaped crystals.

Lead iodide,  $\text{PbI}_2$ , is formed similarly to the chloride as a yellow precipitate. It dissolves in boiling water, depositing on cooling in the form of glittering golden-yellow crystals ('spangles').

Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , is deposited in anhydrous milky-white octahedral crystals from a solution of lead, litharge, or lead carbonate in dilute nitric acid (Libavius, 1595). Concentrated nitric acid precipitates it from aqueous solutions, and lead is not dissolved by the concentrated acid because a protective coating of nitrate is formed. On heating, the crystals decrepitate and evolve nitrogen dioxide and oxygen (p. 397).

Lead sulphate,  $\text{PbSO}_4$ , which occurs as the mineral *anglesite*, is obtained as a white precipitate on adding dilute sulphuric acid or a soluble sulphate to a solution of lead nitrate.

An important lead salt is the acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , known as *sugar of lead* on account of its sweet taste. It is poisonous. Lead acetate is prepared by dissolving lead oxide ( $\text{PbO}$ ) or carbonate in hot dilute acetic acid followed by evaporation and crystallisation. Excess of lead oxide must not be added, otherwise a sparingly soluble basic salt is formed. (The same applies to the preparation of the nitrate.) By boiling litharge with a solution of lead acetate, a solution of a basic acetate, called *Goulard's extract* is formed, which is used as a lotion.

Lead carbonate,  $\text{PbCO}_3$ , is given as a heavy white crystalline precipitate, when a solution of a carbonate is added in the cold to a solution of a lead salt. The basic carbonate,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , is prepared as a white pigment, known as *white lead*. Good white lead is an *amorphous* powder, consisting of minute globules ; it mixes readily with linseed oil, and has a great

covering power. White lead is readily blackened by sulphuretted hydrogen in the atmosphere. Its adulteration by the cheaper barium sulphate is detected by the insolubility of the latter in dilute nitric acid. *Venetian white* is a mixture of equal parts of white lead and barium sulphate; in *Dutch white* the proportions are one to three.

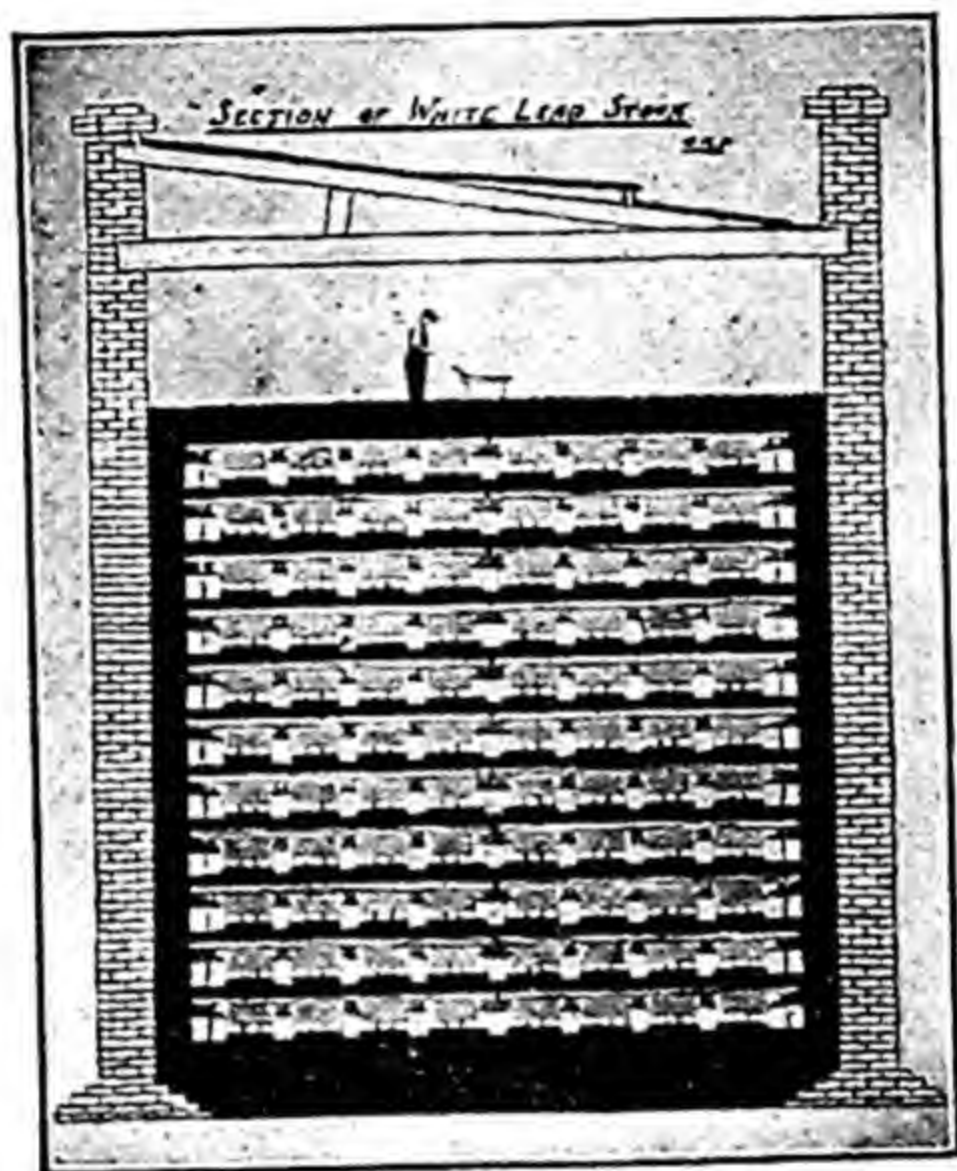


FIG. 375.—SECTION OF WHITE LEAD STACK.

The old so-called *Dutch process* (described by Theophrastos, p. 62) produces a white lead of excellent quality, but is tedious. Lead plates, rolls, or grids, are placed in earthenware pots, with vinegar below. The pots are loosely closed and stacked in rows, covered with planks, interstratified with spent tan-bark, the decomposition of which keeps the pots warm and produces carbon dioxide. Basic lead acetate is probably first produced, and is then decomposed by the carbon dioxide, the acetic acid set free again entering into reaction.

**\*Paints.**—White lead is a pigment, used in the manufacture of paints. Paints generally consist of (1) the *finely ground pigment* mixed with (2) a *drying oil*, chiefly linseed oil, which oxidises on exposure to air and becomes solid, together with (3) a *thinner*, such as turpentine, benzene, or petrol, and (4) a *drier* (or *siccative*), such as litharge, or manganese salts, to accelerate the oxidation



of the oil. The following are the main pigments used for paints :

**White** : white lead ; zinc oxide (*Chinese white*) ; lithopone (p. 601) ; titanium oxide mixed with barium sulphate. Barium sulphate, China clay, etc., are ' fillers ' or ' extenders,' and are of the nature of adulterants, since they have poor covering power.

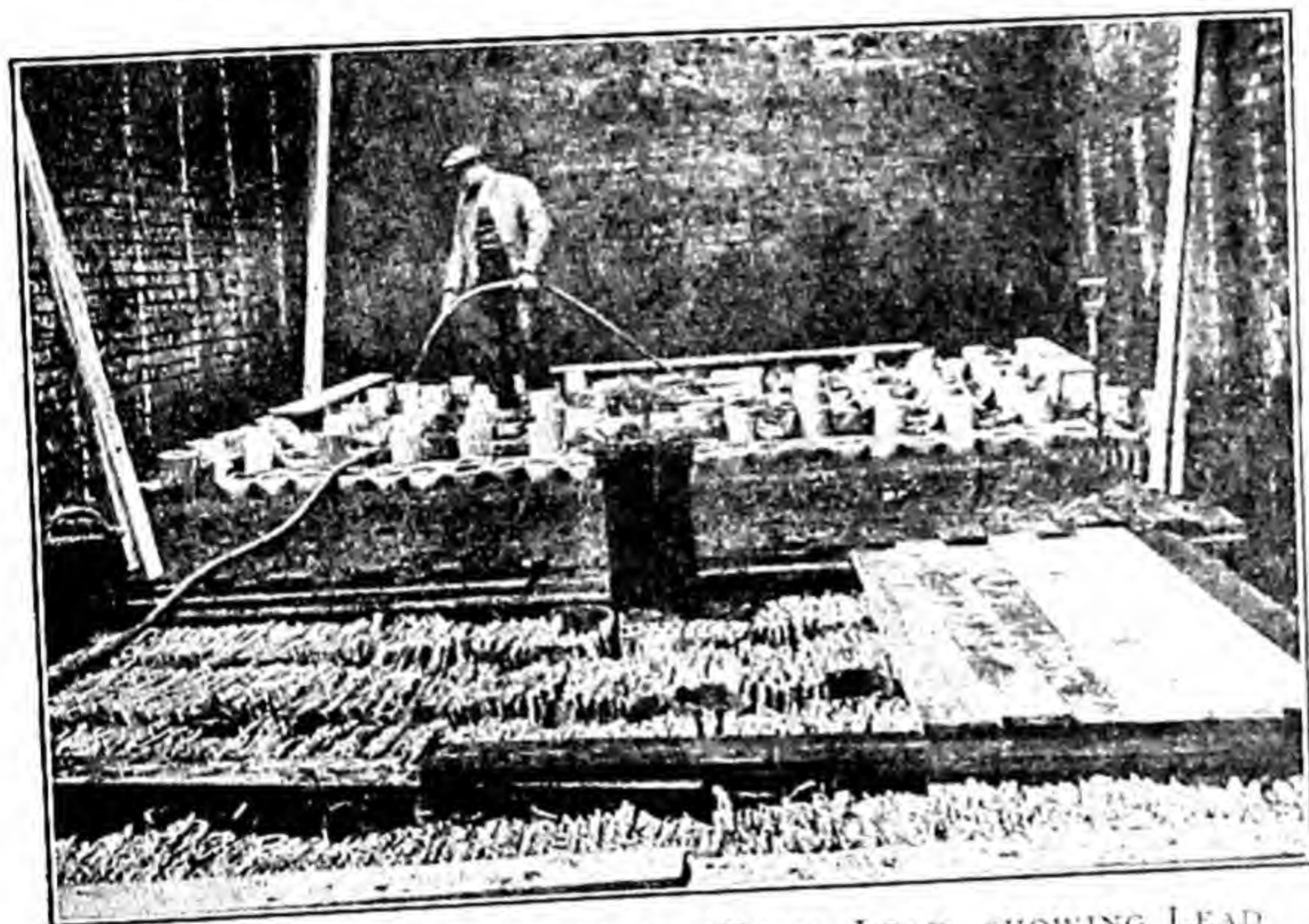


FIG. 376.—MANUFACTURE OF WHITE LEAD, SHOWING LEAD PLATES AND VINEGAR POTS.

(By courtesy of Messrs. Locke, Lancaster, Johnson & Sons, Ltd., manufacturers of ' J ' Brand English White Lead and Paint.)

**Yellow** : ochre (a yellow earth containing hydrated ferric oxide) ; lead chromate ; cadmium sulphide ; lead antimoniate (*Naples yellow*).

**Red** : calcined ochre ; iron oxide (*Indian red* and *Spanish red oxide*) ; rouge (calcined iron oxide) ; lakes of organic dyes, such as madder or alizarin lake ; *vermilion* or *cinnabar*, mercury sulphide,  $\text{HgS}$ .

**Green** : *terre verte* (a natural impure ferric silicate, used in classical times) ; malachite ; copper compounds, such as *verdigris*, *Scheele's green* (little used), and *Schweinfurt*

*green* (an arsenite and acetate of copper); *Brunswick green* (a mixture of Prussian blue and lead chromate); chromium sesquioxide (various varieties).

**Blue**: Prussian blue; ultramarine; glass coloured with cobalt oxide (*smalt*).

**Brown**: *Vandyke brown* (a carbonaceous pigment); *burnt sienna* (a calcined ochre).

**Black**: lampblack and other varieties of amorphous carbon.

In **water colours** the pigments are mixed with glycerin and gum (*e.g.*, gum arabic).

### \*TIN. ANTIMONY. BISMUTH.

**Tin**.—The metal tin must have become known to the early Egyptians and Babylonians, since they used it to make the alloy bronze, but where they obtained it is still a mystery (p. 18).

Tin occurs mainly as the **dioxide**,  $\text{SnO}_2$ , *tinestone*, or *cassiterite*. This is roasted and reduced with carbon to form the metal. Metallic tin is a white crystalline metal which can be rolled into *tin foil*. Tin (*e.g.*, tin foil) emits a peculiar crackling sound when bent; in this way it is easily distinguished from lead. At low temperatures the silver-white metal crumbles to a grey powder, which is an allotropic form (*grey tin*, p. 57). Tin does not tarnish in moist air and is therefore used to make *tinplate*, which is produced by dipping clean iron sheets into molten tin. If the iron becomes exposed, it rusts very rapidly, since the tin and iron in presence of water form a voltaic cell, and the iron is the metal which dissolves. Tin is also used in making bronze, solder (tin and lead), and pewter and Britannia metal (tin, copper, and antimony).

Tin forms two series of compounds (*cf.* copper): **stannous** (*e.g.*,  $\text{SnCl}_2$ ,  $\text{SnO}$ ) and **stannic** (*e.g.*,  $\text{SnCl}_4$ ,  $\text{SnO}_2$ ). **Stannic chloride**,  $\text{SnCl}_4$ , is a fuming liquid formed by the direct union of tin with chlorine, and its formation is utilised in *detinning* tinplate scrap by treating it with chlorine gas. The stannic chloride is used as a mordant and in 'weighting' silk (p. 501). Tin dioxide is used in enamels and glazes.

**Antimony and bismuth**.—Antimony occurs as the sulphide, *stibnite*,  $\text{Sb}_2\text{S}_3$ . The metal, which remotely resembles phosphorus in its chemical properties (*e.g.*, in forming a gaseous hydride,  $\text{SbH}_3$ ) is crystalline, brittle and easily powdered. It is used as a constituent of some useful alloys, such as type metal (70 lead: 20-25 antimony: 2-10 tin) and Britannia metal. The



alloys expand on solidification and give sharp castings. *Tartar emetic*, which is used in medicine and in dyeing, is an antimony potassium tartrate, in which the antimony is present as a radical  $\text{SbO}$ . Precipitated sulphide of antimony is red and is sometimes added to rubber.

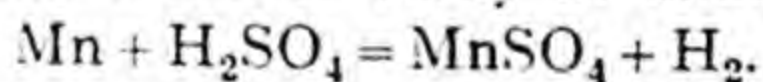
Bismuth is a crystalline metal with a reddish tinge and a low melting point ( $271^\circ$ ). It is a constituent of some fusible alloys, *e.g.*, Wood's metal, which melts at  $60.5^\circ$  and is used in offices, warehouses, etc., in water sprinklers which operate automatically in case of fire by the fusing of a plug. The basic nitrate of bismuth ('bismuth subnitrate') is used in medicine and as a cosmetic: it is a white powder.

## CHAPTER XXXVII

### MANGANESE AND CHROMIUM

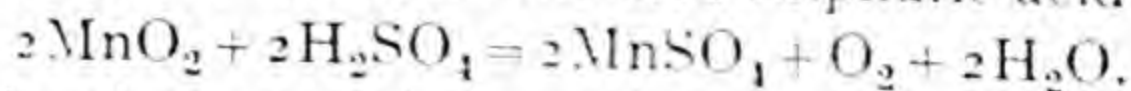
**Manganese.**—The most important ore of manganese is the black dioxide,  $\text{MnO}_2$ , known as *pyrolusite*, referred to by Pliny as 'magnes,' but confused with an ore of iron, the magnetic oxide,  $\text{Fe}_3\text{O}_4$ . The name *pyrolusite* (Greek *pyr*, fire; *luo*, I dissolve) refers to the use of the mineral in decolorising glass (p. 596).

Metallic manganese is obtained by reducing the oxide with carbon at a high temperature, or by aluminium in the thermit process. It is greyish-white, hard, and brittle, not oxidised in air when pure, and dissolves easily in dilute acids, evolving hydrogen :

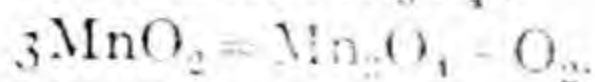


Alloys of iron and manganese, obtained in the blast furnace, are *ferromanganese* (70-80 per cent. of manganese and less than 0.3 per cent. carbon, for open-hearth steel) and *spiegel* (20-32 per cent. of manganese and more than 0.3 per cent. of carbon, for Bessemer steel); *manganese steel*, which may contain up to 13 per cent. of manganese, is very hard and tough. It is used for the jaws of rock-crushers, and for machinery. *Manganese bronze* is copper alloyed with variable amounts of manganese and zinc. Alloys of copper and zinc with small quantities of manganese resemble German silver. *Manganin* is an alloy of 83 parts of copper, 13 of manganese, and 4 of nickel. It is used for resistance coils, since its electrical resistance is only slightly affected by temperature.

**Manganese dioxide**,  $\text{MnO}_2$ , is used as an oxidising agent, and in Leclanché cells (*q.v.*). It evolves oxygen and forms manganous sulphate when heated with concentrated sulphuric acid :



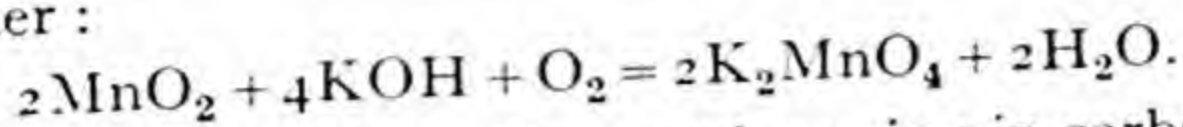
The dioxide when strongly heated alone evolves oxygen and leaves a residue of a red oxide,  $\text{Mn}_2\text{O}_3$  :



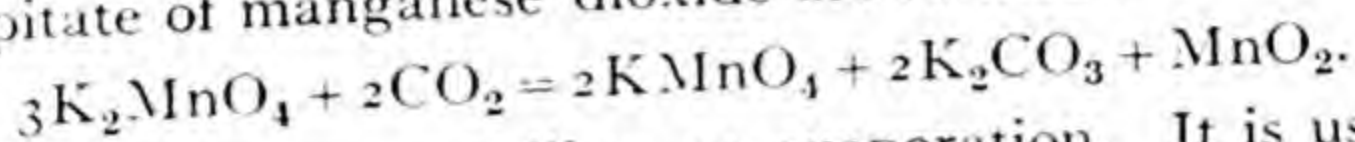
With concentrated hydrochloric acid it evolves chlorine (p. 312).



On fusing manganese dioxide with potassium hydroxide and potassium nitrate or chlorate, in presence of air, **potassium manganate**,  $K_2MnO_4$ , is formed, which gives a green solution with a little water :

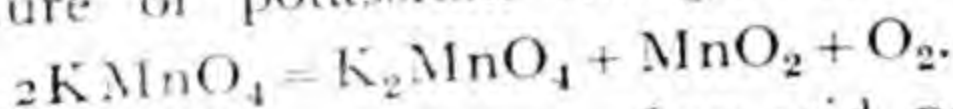


On diluting the solution, boiling and passing in carbon dioxide, a purple-red solution of **potassium permanganate**,  $KMnO_4$ , and a precipitate of manganese dioxide are formed :

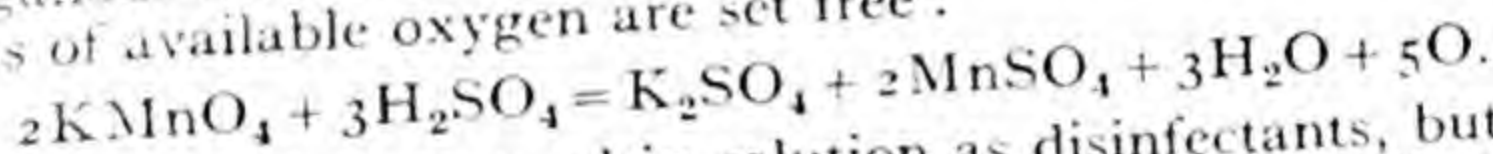


The permanganate crystallises on evaporation. It is used as a disinfectant and oxidising agent.

On heating, potassium permanganate evolves oxygen and leaves a mixture of potassium manganate and manganese dioxide :

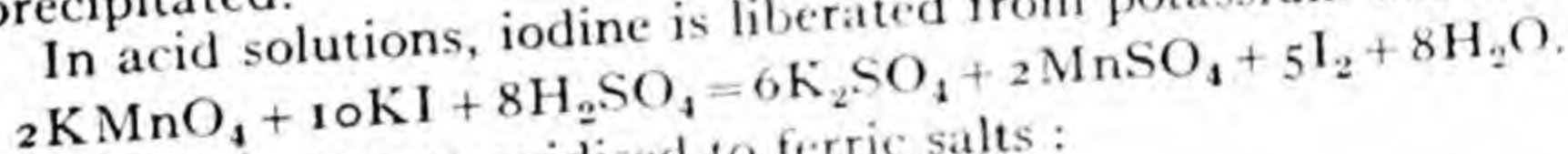


In solution, especially in presence of an acid, permanganate is a powerful oxidising agent. The manganese is reduced to a manganous salt, and from two molecules of permanganate, five atoms of available oxygen are set free :

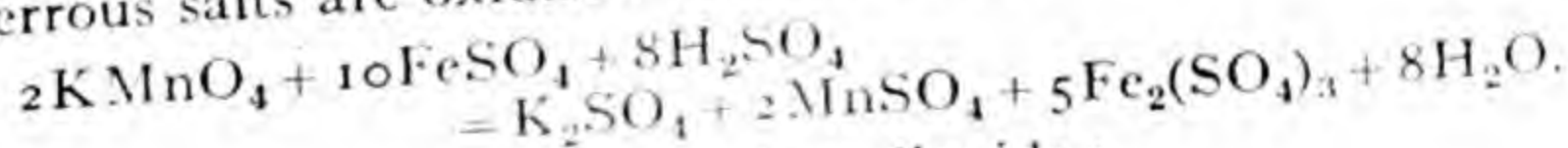


Permanganates are used in solution as disinfectants, but they have the objection that brown hydrated manganese dioxide is precipitated.

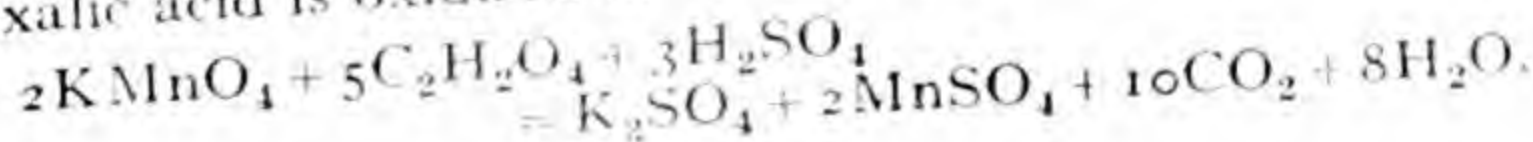
In acid solutions, iodine is liberated from potassium iodide :



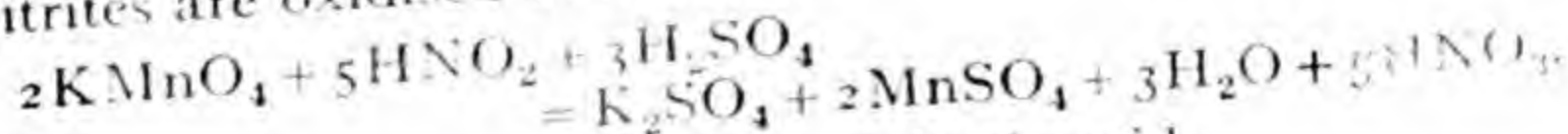
Ferrous salts are oxidised to ferric salts :



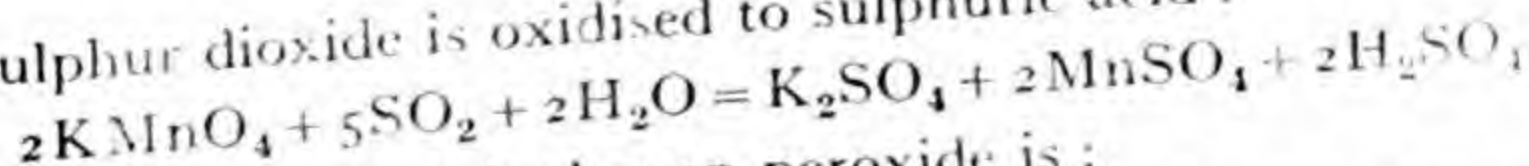
Oxalic acid is oxidised to carbon dioxide :



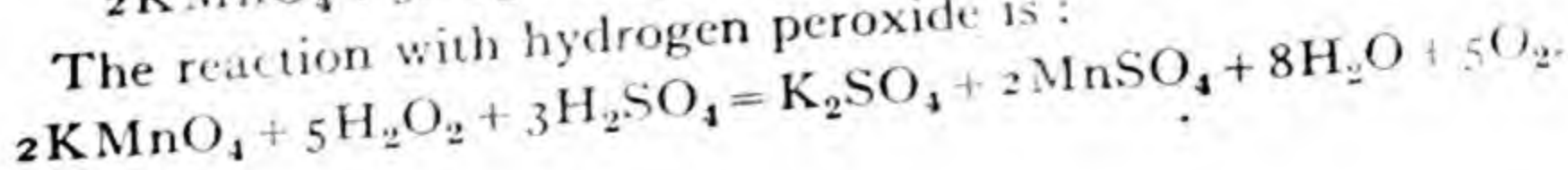
Nitrites are oxidised to nitrates :



Sulphur dioxide is oxidised to sulphuric acid :

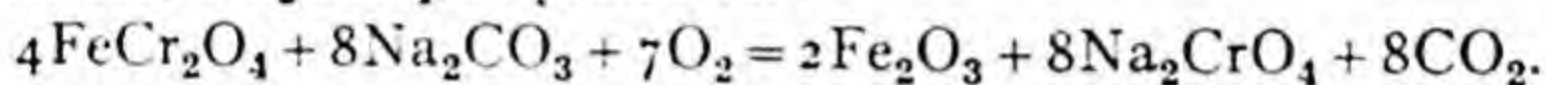


The reaction with hydrogen peroxide is :

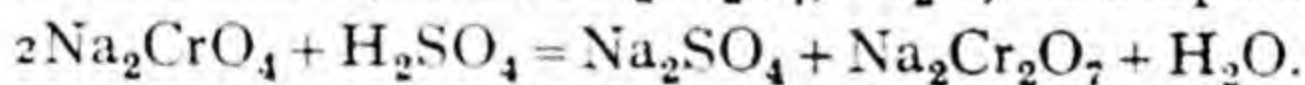


**Chromium.**—The commonest ore of chromium is *chromite*, or *chrome-ironstone*,  $\text{FeCr}_2\text{O}_4$  or  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . This is very refractory and is made into chrome bricks used for furnace linings, or to separate the silica bricks outside from the magnesia bricks inside the basic hearth steel furnace (*q.v.*). Chromite is the source of chromium compounds. If reduced in the electric furnace, **ferrochrome**, iron with 60-70 per cent. of chromium, is formed, which is used in the manufacture of *chrome steel*. It is not attacked by acids. An alloy of chromium, nickel, and iron is used for making armour plates. *Stainless steel* is ordinary steel with 12-14 per cent. of chromium and up to 0.7 per cent. of nickel. *Stellite* (p. 566) contains chromium.

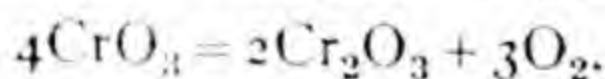
When powdered chromite is heated to bright redness with sodium carbonate and a little lime in contact with air, sodium chromate,  $\text{Na}_2\text{CrO}_4$ , is produced :



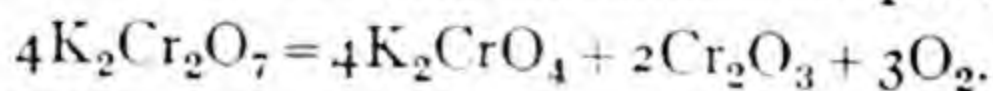
Sodium chromate forms a yellow solution in water which, on treatment with sulphuric acid, deposits sodium sulphate and gives a red solution containing **sodium dichromate**. This deposits in red deliquescent crystals,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , on evaporation :



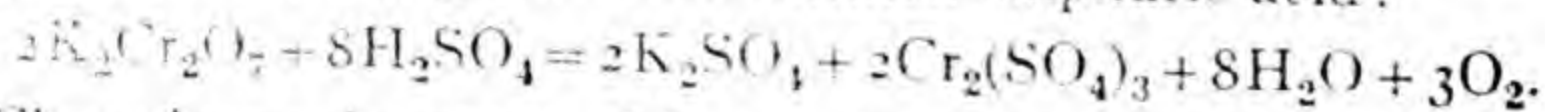
**Potassium dichromate**,  $\text{K}_2\text{Cr}_2\text{O}_7$ , crystallises better than the sodium salt. By the action of concentrated sulphuric acid on solutions of sodium or potassium dichromates in the cold, red needle-shaped crystals of **chromium trioxide**,  $\text{CrO}_3$  (commonly called 'chromic acid'), are obtained. This is a very powerful oxidising agent. On heating, it decomposes, evolving oxygen and leaving green insoluble chromium sesquioxide :



Potassium dichromate when *strongly* heated evolves oxygen, leaving potassium chromate and chromium sesquioxide :



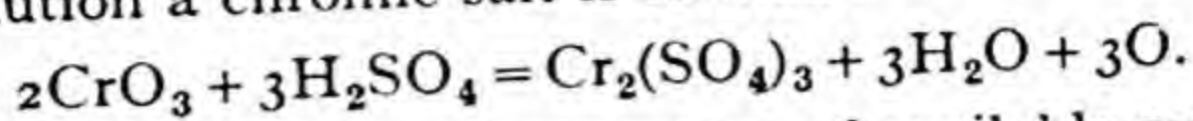
Potassium dichromate evolves oxygen and forms an olive-green mass containing chromic sulphate and potassium sulphate, on heating with concentrated sulphuric acid :



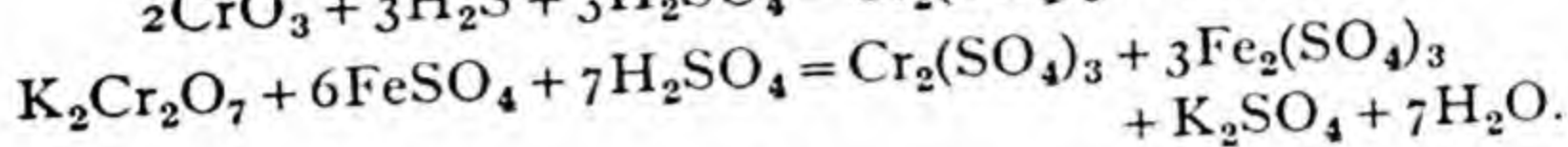
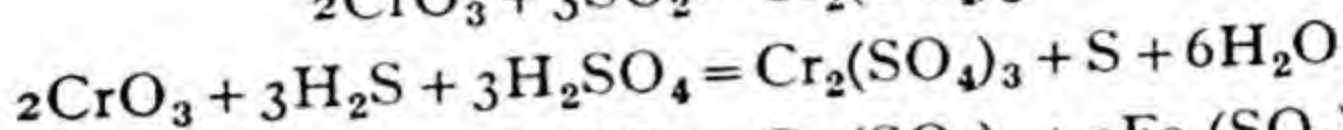
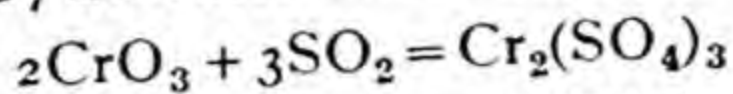
Chromium salts are used in tanning leather, the green sesquioxide,  $\text{Cr}_2\text{O}_3$ , is used as a pigment, and the bright yellow lead chromate is used for paints, either alone or (for green paint) mixed with Prussian blue.



Chromic acid and dichromates are used as oxidising agents : in acid solution a chromic salt is formed :



Thus  $\text{K}_2\text{Cr}_2\text{O}_7$  liberates three atoms of available oxygen.



**Metallic chromium** is obtained as a white metal by the thermit process from chromium sesquioxide and aluminium, or (as in chromium plating) by electrolysis.

**Chrome alum**,  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , is isomorphous with common alum (p. 187).

**\* The utilisation of metals.**—The earliest chemical operations known to man, carried out at least as early as 4000 B.C., were concerned with the production of metals, since the earlier working of pottery could scarcely be described as one involving important chemical reactions (see p. 12). During the earliest period copper was in use, followed by bronze and later by iron. The last-named metal continued in general use as the commonest metal for many centuries, and almost until the beginning of the twentieth century copper, bronze, brass and iron were the only common metals in daily use. In the Paris Exhibition of 1855 aluminium was shown as a curiosity. During later years many other metals previously regarded as rare have come into use. Alloys of magnesium and aluminium and of iron with such metals as cobalt, tungsten, vanadium and molybdenum are now all made and put to various uses. It is very probable that advances in chemistry will lead to the use of other metals now scarcely ever seen; for example, in the last few years the 'rare' metal beryllium has come into use in small quantities.

As compared with the progress made in the use of metals from 4000 B.C. to about A.D. 1850, the advances made possible by modern chemistry during the recent century are really impressive, and there is no reason to suppose that this progress will not be maintained. The advances in engineering, the construction of high-speed motors, and aircraft, have all been made possible by the co-operation of the chemist in the production of light and strong alloys.

# QUESTIONS

## PART III

### ORGANIC CHEMISTRY

1. What is soap? Can soap be prepared from kerosene oil? Describe briefly the manufacture of soap. [Allahabad Inter.]

2. What are kerosene oil, vaseline, and glycerin? Write a short note on the kerosene oil industry. [Allahabad Inter.]

3. What do you understand by *combustion*? Give examples. Describe experiments which show that the terms combustible substance and supporter of combustion are only relative. State the approximate composition of gunpowder, and account for the explosive nature of this substance. [London Gen. School.]

4. What are the principal elements which enter into the composition of organic bodies? Describe how you would experimentally prove the presence of any *three* of these elements in a given organic body such as the white of egg. [Central Welsh Board, Elementary.]

5. Of what elements is starch composed? Explain how starch may be brought into solution in water. Name *three* common foodstuffs which contain starch, and explain how you would show starch to be present in them. [Central Welsh Board, Elementary.]

6. From what materials are candles made? Describe as fully as possible the stages in the process when a candle burns, and illustrate your answer by reference to a diagram of the candle flame. [Queen's Univ. Belfast Matric.]

7. What forms of sugar occur in daily life? How is glucose obtained from starch? In what ways does glucose differ from cane sugar?

8. What is cellulose? What common materials consist mainly of cellulose? How would you obtain a specimen of pure cellulose from one of these?

9. What important products are made from cellulose? Why is the name "artificial silk" not a suitable one from the chemical point of view?

10. How do silk and wool differ chemically from cotton and flax? How may cotton be separated from a mixture of cotton and wool?



11. Give an account of the fermentation of sugar and explain how strong alcohol is obtained from the product. What are the technical uses of alcohol? What is methylated spirit?
12. What is an enzyme? What important chemical changes are brought about by enzymes?
13. What common organic acids are used in daily life? What characteristic grouping of atoms is present in all organic acids?
14. How is vinegar made? How would you obtain acetic acid from vinegar? From acetic acid how would you obtain marsh gas?
15. How is tartaric acid obtained? What are the optical properties of the tartaric acids and to what are they supposed to be due?
16. What are the constituents of oils and fats? How would you test a candle in order to find if it is a stearin candle or a paraffin candle?
17. How is glycerin made on the large scale? For what purposes is glycerin used?
18. What valuable materials are contained in coal tar? How are they separated and for what purposes are they used?
19. Describe the composition and uses of the common explosives.
20. What is a dye? What natural dyes are used? What natural dyes have largely been replaced by synthetic materials?
21. Explain the meaning of the terms: substantive dye, adjective dye, mordant, vat dye, chromophore, quinonoid grouping.
22. What are essential oils? How are they obtained?
23. What is rubber? What treatment is applied to raw rubber in order to make it useful?
24. How is leather made from skins?
25. Classify foods according to their functions. What is meant by the energy value of a food and how is it determined?
26. What are vitamins? Explain their importance in diet.
27. Describe the various changes which occur in the body during the digestion of (a) starch, (b) lean meat, (c) milk.
28. In what way can micro organisms produce disease? How is their activity prevented (a) outside the body, (b) in the body? What is the difference between a disinfectant and an antiseptic?
29. What is formalin? What important products are obtained from it?
30. How is acetone manufactured and for what purposes is it used?
31. How is chloroform prepared and purified? How can it be shown that chloroform contains chlorine? What products are formed when chloroform undergoes oxidation?

[Conjoint Medical Board.]

32. How is ethylene prepared? What compounds does it form with (a) bromine, (b) sulphuric acid, (c) hydriodic acid?

[Conjoint Medical Board.]

33. Acetic acid and lactic acid on analysis give the same empirical formula. What is this formula? Mention any other substances with the same empirical formula. Describe, *in detail*, one method of determining the molecular weight of any of these compounds.

[Conjoint Medical Board.]

34. Describe the isolation of phenol from coal tar. What is the action of (a) bromine, (b) nitric acid, (c) caustic soda, upon phenol?

[Conjoint Medical Board.]

35. What do you understand by the empirical formula of a compound? Knowing the empirical formula of a non-volatile compound which is soluble without change in benzene, how would you determine the molecular formula of the compound?

[Conjoint Medical Board.]

36. Describe a method of obtaining an aqueous solution of acetaldehyde. By what tests would you identify such a solution?

[Conjoint Medical Board.]

37. A dibasic organic acid was found to contain 32.0 per cent. of carbon and 4.0 per cent. of hydrogen. Calculate the empirical formula of the acid. The silver salt was found to contain 59.3 per cent. of silver. Calculate the molecular weight of the acid and write down its structural formula.

[Conjoint Medical Board.]

38. By what different agents can a fat be hydrolysed? Write down the equation for the action of sodium hydroxide on a typical fat. From the products of this reaction describe how you would obtain a crystallised specimen of the fatty acid.

[Conjoint Medical Board.]

## METALS

1. Write a short essay on the uses of metals in daily life.

2. What is meant by the following terms: ore, gangue, flotation, roasting, flux, smelting, refining?

3. You are given three pieces of metal. One is covered with a green crust, one with a white crust, and one with a brown crust. What metals (or alloys) would you expect these to be, and what further observations or tests could you apply to distinguish them?

4. Draw up a classification of the common metals based on their action on water in different circumstances and compare the result with the periodic classification.

5. Draw up a table exhibiting the action of (a) air, (b) water, (c) dilute sulphuric acid, (d) concentrated hydrochloric acid, (e) dilute nitric acid, on the following metals: sodium, aluminium, iron, tin, lead.

6. What metals are dissolved by hot caustic potash solution? What products are formed?



7. Illustrate, by reference to two chemical and to four physical properties, the chief differences between the metals and the non-metals. Describe briefly how a metal may be isolated from (a) a naturally occurring sulphide and (b) a naturally occurring carbonate. [Joint Matric.]

8. Explain with illustrations the chief characteristics by which metals may be distinguished from non-metals. [Oxford and Camb. School Cert.]

9. What *chemical* properties distinguish metals as a class? Give three distinct methods by which metals may be converted into their oxides. Illustrate your answer with reference to copper, magnesium, and zinc respectively. How may the oxides of magnesium and zinc be distinguished from each other? [London Gen. School.]

10. Give four methods by which metals are obtained from their native sources. [Queen's Univ. Belfast, Entrance Schol.]

11. What is observed when the following metals are left exposed to the action of the atmosphere for a considerable time: (a) sodium, (b) iron, (c) lead, (d) zinc? State briefly what tests you would carry out in order to prove that the reactions are as you describe. [Central Welsh Board, Elementary.]

12. Give briefly the principal methods employed for the extraction of metals from their ores. Illustrate your answer by reference to the extraction of tin, chromium, and sodium. [Central Welsh Board, Higher.]

13. Describe the manufacture of common salt and briefly mention the industries where common salt forms the raw material for the manufacture of other important compounds. [Mysore Entrance.]

14. Describe some method for the preparation of sodium hydroxide on a commercial scale. Give an account of the properties of this substance, and state how it reacts with (a) chlorine, (b) phosphorus, (c) zinc, (d) ferrous sulphate.

15. Starting with metallic sodium, how may specimens of the following be prepared: (a) sodium hydroxide, (b) sodium carbonate, (c) sodium bicarbonate, (d) sodium sulphate, (e) sodium peroxide. What is the action of heat upon a (i) acid of water upon (c)? [London Matric.]

16. By what methods are metallic carbonates usually prepared? Give examples. What is the effect of heat upon (a) normal carbonates, (b) bicarbonates. Three grams of a mixture of anhydrous sodium carbonate and sodium bicarbonate lost 0.348 gram on heating. Calculate the percentage of anhydrous sodium carbonate in the mixture. [London Gen. School.]  
(Na = 23, C = 12, O = 16)

17. Starting from sodium hydroxide, describe exactly how you would prepare solid specimens of (a) normal sodium carbonate, (b) acid sodium carbonate, (c) acid sodium sulphate, (d) neutral sodium sulphate. [London Matric.]

18. Make a list of sodium salts which evolve gas (a) with dilute sulphuric acid, (b) with concentrated sulphuric acid. Write the formulae for the gases, and indicate briefly how you would test each with a view to ascertaining the nature of the original salt. [Madras Inter.]

19. Describe how washing soda is obtained and how caustic soda is prepared from it. Explain clearly how the composition of caustic soda has been ascertained by the synthesis of the substance. State clearly the similarities and differences between caustic soda and washing soda. [Madras S.L.]

20. What are the differences in properties between sodium carbonate and sodium bicarbonate? How could you convert one into the other? How would you prepare a specimen of sodium carbonate? [Madras Inter.]

21. How may sodium hydroxide be prepared? How does this substance react with (a) carbon dioxide, (b) ammonium chloride? [Camb. Local Jun.]

22. Describe, with experimental details, the processes you would use to demonstrate the truth of the following statements:

- (a) Lime contains oxygen;
- (b) Carbon dioxide contains carbon;
- (c) Nitric acid contains hydrogen;
- (d) Caustic soda contains hydrogen.

23. How is quicklime manufactured? How would you obtain from it (a) slaked lime, (b) milk of lime, (c) lime water? State their uses. [Calcutta Inter.]

24. What happens when (a) hydrogen is passed over heated iron oxide; (b) limestone is heated in an iron tube; (c) carbon dioxide is passed over heated charcoal; (d) steam is passed over heated iron? Explain the chemical changes fully. [Madras S.L.]

25. Describe the changes observed and name the product or products formed when

- (a) Concentrated sulphuric acid is heated with charcoal.
- (b) Mercury is ground up with sulphur.
- (c) A concentrated solution of caustic potash is saturated with chlorine gas.
- (d) Copper is treated with dilute nitric acid.
- (e) Copper sulphate crystals are placed in concentrated sulphuric acid. [Travancore S.L.C.]

26. Describe in detail, with a sketch of the apparatus used, a laboratory method for the preparation of bleaching powder. What is its probable composition? How would you prepare from this bleaching powder (a) oxygen, (b) chlorine? [London Matric.]

27. Give an account of the occurrence of aluminium in Nature, and the method by which the metal is manufactured. Describe its chief physical and chemical properties. What are its useful alloys? [Punjab Univ.]



**28.** How is calcium carbide usually prepared? Explain carefully how this substance may be used for the purpose of rendering atmospheric nitrogen into a usable form. [Central Welsh Board, Higher.]

**29.** Compare the properties of the alkali metals with those of the alkaline earths. An intimate mixture of calcium carbonate and magnesium powder containing 16 per cent. of calcium carbonate is given to you. What volume of normal hydrochloric acid would you require just to dissolve 0.5 gram. of the mixture and what volume of gas at N.T.P. would be evolved in the process of solution? [Madras Inter.]

**30.** You are given a mixture of calcium and magnesium carbonates. 1.84 gm. of the mixture are ignited until no further loss of weight takes place. The residue weighs 0.96 gm. What is the percentage composition of the mixture and what volume of  $\text{CO}_2$ , measured at  $30^\circ \text{C}$ . and 750 mm., is evolved during the ignition? [Madras Inter.]

**31.** What is the composition of brass? How would you proceed to find out whether brass is a mixture or a chemical compound? [Travancore S.L.C.]

**32.** Describe the more important methods for preparing salts and illustrate your answer by giving the methods for the preparation of the following salts: ammonium chloride, zinc sulphate, magnesium sulphate, potassium sulphate, calcium nitrate, potassium bicarbonate. [London Matric.]

**33.** You are given a mixture of zinc and zinc oxide. State precisely how you would proceed, guided by previous experience, to determine the percentage of each constituent of the mixture. [Madras S.L.]

**34.** Describe as fully as possible how pure zinc may be prepared from the ore zinc sulphide. [Queen's Univ. Belfast Matric.]

**35.** Enumerate the chief general characteristics of the metals. Given metallic zinc, how would you prepare moderately pure specimens of zinc sulphate, zinc oxide, and zinc carbonate? [Central Welsh Board, Elementary.]

**36.** Name two metals with which sulphur can be caused to combine directly. Explain how combination can be brought about and how in each case it can be established that chemical combination has taken place. [London Matric.]

**37.** State and explain all the reactions observed in the following circumstances:

- A piece of bright copper is heated with concentrated sulphuric acid.
- The liquid product of (a) is carefully added to a quantity of cold water.
- The gaseous product of (a) is passed into a solution of hydrogen sulphide.
- Zinc is added to a slightly acidified solution of ferric chloride.
- A piece of charcoal is dropped into a solution of sulphuric acid.
- Zinc is placed in an aqueous solution of ferric sulphate. [London Univ. School]

38. Starting from metallic copper, how would you prepare a crystalline specimen of copper sulphate? Describe what you would observe on adding (a) iron, (b) sodium hydroxide, to an aqueous solution of copper sulphate.

39. Describe in some detail two distinct methods by which metallic copper may be obtained from copper sulphate. Write down the formula for crystallised copper sulphate and describe the action of heat on this substance. [London Gen. School]

40. Starting from pure copper, how would you prepare moderately pure specimens of (a) cupric sulphate, (b) cupric oxide, (c) cupric chloride, (d) cupric sulphide? Describe carefully the appearance of each product. [London Matric.]

41. If you were supplied with metallic copper, how would you prepare the following compounds: cupric sulphate, cupric chloride, cuprous oxide? Describe the appearance of each of these substances and the effect, if any, of potassium hydroxide on each. [Madras Inter.]

42. Compare the chief physical and chemical properties of sodium and copper. Briefly describe the preparation by the use of the electric current, (a) of sodium from caustic soda, (b) of copper from copper sulphate. [Joint Matric. Board.]

43. How would you prepare specimens of each of the following substances: (a) copper carbonate, given copper sulphate, (b) nitric acid, given zinc nitrate, (c) ammonia gas, given ammonium chloride? [Joint Matric.]

44. What happens when air is allowed to have free access to each of the following substances: (a) sodium, (b) calcium chloride, (c) nitric oxide, (d) quicklime, (e) sodium carbonate decahydrate? [Camb. School Cert.]

45. Explain the chemistry of the extraction of copper from its sulphide. Describe and explain the preparation of the following compounds of copper: (a) cupric chloride, (b) cuprous oxide, (c) cuprous chloride. How does (b) react with the dilute mineral acids? [Central Welsh Board, Higher.]

46. What is the effect of strongly heating:

*Either* (a) (i) ammonium alum; (ii) silver nitrate; (iii) ammonium phosphate;

*or* (b) (i) ferrous sulphate; (ii) lead nitrate; (iii) disodium hydrogen phosphate? [Madras S.L.]

47. Name an ore of iron and give its composition. Describe the preparation of green vitriol from iron. How is iron obtained from the salt prepared? [Madras S.L.]

48. Describe in detail how you would obtain a specimen of pure crystallised ferrous sulphate if you were given some sulphuric acid and iron nails. [Camb. Local Jun.]



**49.** Iron is said to form two *series* of salts. Explain what is meant by this statement. Describe how you would prepare from metallic iron one member of each of these series. [Camb. Local Sen.]

**50.** What evidence can you give for the wide distribution of iron in Nature? Name and give the formulae of two iron ores. What do you understand by the smelting of iron ore? What two series of compounds does iron form? Write down the formulae for the chlorides, sulphates and nitrates of these iron compounds. [Queen's Univ. Belfast, Matric.]

**51.** Write a short account of the properties of the three chief varieties of iron. Explain the peculiar smell noticed when iron filings are dissolved in hydrochloric acid. State *two* methods for converting a ferrous salt into a ferric salt. [Central Welsh Board, Elementary.]

**52.** By what tests would you distinguish between ferrous and ferric salts? Why do not potassium ferrocyanide and potassium ferricyanide respond to these tests? [Central Welsh Board, Higher.]

**53.** If you were provided with iron filings, what experiments would you make to show that iron forms two series of salts—ferrous and ferric salts? [Oxford and Camb. School Cert.]

**54.** Explain the chemical and physical changes, if any, which may be observed when equal quantities of normal solutions of the following are gradually mixed in the order given:

(1) Caustic soda, hydrochloric acid and silver nitrate.  
or

Sodium carbonate, nitric acid and silver nitrate.

(2) Ferric chloride, caustic potash and hydrochloric acid.

(3) Copper sulphate, ammonia and sulphuric acid,  
or

Copper sulphate, ammonia and caustic soda.

[Mysore Entrance.]

**55.** Starting with metallic iron, how would you prepare (a) ferrous sulphate crystals, (b) ferric oxide, (c) ferric chloride? Discuss the action of heat on (a). [London Matric.]

**56.** Can you prove that (i) paper contains carbon; (ii) nitre contains oxygen; (iii) ferrous sulphate contains iron? [India U.P.]

**57.** What is the difference between carbon and charcoal? (2) marble and chalk. (3) iron ore and iron oxide? [India U.P.]

**58.** What are the principal industrial compounds of iron? What is the nature of the principal chemical reactions which take place in the various zones of the blast furnace? [Madras Univ.]

**59.** What happens when (a) nitre is strongly heated in a hard glass tube; (b) burning magnesia is put into a jar of hydrogen gas; (c) iron filings are left in water containing a little of green vitriol is gradually heated to reduce iron? [India U.P.]

60. How may the following elements be obtained from their oxides : carbon, lead, hydrogen, phosphorus ? [London Matric.]

61. Mention two compounds which occur in Nature of *one* of the following metals : (i) zinc ; (ii) tin. Describe how the metal can be obtained from either compound. Mention the uses of the metal in everyday life. Mention two compounds of the metal and describe how they are prepared from it. [Madras S.L.]

62. Write an account of the oxides of lead. How does hydrochloric acid react with (a) red lead, (b) lead monoxide ? [Camb. Local Jun.]

63. Describe, giving full experimental details, how you would prepare (a) potassium from potassium hydroxide, (b) lead from litharge, (c) copper from copper sulphate crystals. [Joint Matric.]

64. Write an historical account, extending to not more than a page and a half, of *either* of the following :

The chemistry of the air.

The classification of the elements.

[School Leaving Certificate (Higher), Scotland.]

65. Represent by equations the undernoted reactions, heat being applied where necessary.

(a) Action of nitric acid on copper, and sulphurous acid.

(b) Action of concentrated sulphuric acid on copper, sodium nitrate, calcium chloride, and oxalic acid.

(c) Action of dilute sulphuric acid on zinc and ferrous sulphide.

(d) Action of heat on lead nitrate and calcium carbonate.

Write the chemical formulae for sodium carbonate, sodium bicarbonate, calcium bicarbonate, ferrous sulphate, ferric sulphate, aluminium chloride. [Educ. Institute of Scotland, Preliminary.]

66. Write a short account of two of the following :

(a) Methods of drying gases ;

(b) Methods of collecting gases ;

(c) Methods of separating gases.

[London Matric.]

67. Write an essay on *one* of the following subjects :

(a) The uses of electricity to the chemist.

(b) Explosions.

(c) The influence of light on chemical reactions.

[Central Welsh Board, Higher.]

68. Write a short essay on what you consider are the principal aims of the science of chemistry and how these aims are effected.

[Queen's Univ. Belfast, Matric.]

69. Write a short account of the manufacture of *one* of the following : sulphuric acid, washing soda, bleaching powder.

[School Leaving Certificate (Higher), Scotland.]

70. What are the principal elements found in plants, and how does the plant obtain each of these during its growth ? Describe exactly



how any two of the constituent elements could be obtained in a reasonable state of purity from a piece of wood. [London Matric.]

**71.** Write a clear explanatory note on *five* of the following : (a) the use of helium in airships ; (b) the use of calcium carbide in cycle lamps ; (c) the effervescence that takes place when a bottle of lemonade is opened ; (d) the use of yeast in bread-making ; (e) the ingredients of gunpowder ; (f) the tarnishing of silver egg-spoons ; (g) the fact that safety matches strike on the box only. [School Leaving Certificate (Higher), Scotland.]

**72.** State briefly one method of preparing each of the following substances : magnesium oxide ; iodine ; sodium chloride ; sulphur trioxide ; sodium hydroxide.

In what class would you place each of these substances ? Give reasons. [School Leaving Certificate (Higher), Scotland.]

**73.** Explain shortly the chemical reactions involved in *five* of the following :

- (1) The blue flame at the top of a clear fire.
- (2) The change in colour when hydrochloric acid and small pieces of zinc are added to a solution of ferric chloride.
- (3) The formation of stalactites.
- (4) The hardening of mortar.
- (5) The disappearance of the colour when chlorine water is exposed to sunlight.
- (6) The disappearance of the odour when coal gas is burned.

[School Leaving Certificate (Higher), Scotland.]

**74.** What do you know about the utilisation of the following waste-products :

- (a) Spent iron oxide and coal-tar of the gasworks ;
- (b) Burnt pyrites of the sulphuric acid works ;
- (c) Calcium sulphide of the alkali works ? [Patna Univ. B.Sc.]

**75.** Write a short account of *one* of the following :

- (1) Manufacture of phosphorus.
- (2) Refrigeration by means of ammonia.
- (3) Manufacture of coal gas for domestic purposes.

[School Leaving Certificate (Higher), Scotland.]

**76.** Shew how any *five* of the following contributed to the development of the Science of Chemistry : Boyle ; Lavoisier ; Dalton ; Cavendish ; Mendeleev ; Madame Curie. [School Leaving Certificate (Higher), Scotland.]

**77.** Write a short essay, extending to not less than a page and a half, on the importance of the chemist in the life of our modern community. [School Leaving Certificate (Higher), Scotland.]

## ANSWERS TO QUESTIONS

### ORGANIC CHEMISTRY.

37.  $C_2H_3O_3$ . 150.  $\begin{array}{c} CH(OH)COOH \\ | \\ CH(OH)COOH. \end{array}$

### METALS.

16. 68.567 %  $Na_2CO_3$ .  
29. 36.6 c.c.  $N$   $HCl$ ; 410.14 c.c. gas at N.T.P.  
30. 45.652 %  $MgCO_3$ ; 54.348 %  $CaCO_3$ .  
150.04 c.c.  $CO_2$  at  $30^\circ$  and 750 mm.



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